

CHEMICAL PROCESSES IN VISCOUS MATERIALS

BY

MARK JAY BARNES

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1989

TO MY FAMILY WHOSE SUPPORT NEVER FALTERED

ACKNOWLEDGEMENTS

The most cherished and remembered things which a person can obtain in his lifetime are those which require sacrifice and dedication to achieve. The pursuit of knowledge is certainly no exception to this definition. If exception be taken with this definition, it is due to the implication that sacrifice and dedication are contributed only by the individual. On the contrary, an education would be impossible to achieve without the sacrifice and dedication of a large number of people.

First and foremost I wish to express my gratitude to my family. Their continued support and encouragement have given me the opportunity to fulfill what was once a dream. My parents, Avery and Marilyn, have instilled in me a sense of security which can never be taken away. From them I have learned what happiness is, from where it comes, and how it can be obtained. To my brothers and sister-in-law, Douglas, Curtis, and Robin, I owe my love of science. It was they who pointed me in the right direction and taught me to never be apprehensive of the unexpected. To my grandparents I am indebted for all their generosity and support.

I would also like to thank my teachers who have instilled in me a love for chemistry, Glenn Vogel, Heinz and Judy Koch, Harry Sisler, and most importantly Russell "Doc" Drago. It is truly an inspiration to

know a person who loves and enjoys his work as much as he does. I would also like to thank Ruth Drago for making Florida my home away from home.

I would also like to thank all of my friends. There are too many to list, but there are those who have influenced me greatly in one way or another. Included in this list are the past and present residents of the "Thunderdome": Todd "Spud" Gillespie, Stephen "Julio" Brooks, Mark "Chin" Hail, Gerald "Citrus Connection" Grunewald, and Donald "Bueller" Ferris. I would also like to extend my gratitude to past and present members of the Drago Group, in particular, Maribel Lisk, Robert Taylor, Larry Chamusco, Edward Getty, Cindy Getty, Shannon Davis, Richard Riley, and especially Ngai Wong, who has been a good friend and source of information for many years. Lastly, I would like to express my gratitude to my girl friend, Kaneez Rizvi. I owe a considerable portion of my sanity to her for the love and understanding she has given me.

TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGEMENTS.....	iii
LIST OF TABLES.....	vi
LIST OF FIGURES.....	viii
ABSTRACT.....	x
CHAPTERS	
I GENERAL INTRODUCTION.....	1
II COBALT(II)-FACILITATED TRANSPORT OF DIOXYGEN IN A POLYSTYRENE MEMBRANE.....	4
Introduction.....	4
Experimental.....	16
Results and Discussion.....	21
III DEMONSTRATION OF THE FEASIBILITY AND VERSATILITY OF MEMBRANE REACTORS.....	43
Introduction.....	43
Experimental.....	58
Results and Discussion.....	62
IV HETEROGENEOUS HYDROFORMYLATION OF PROPYLENE USING SUPPORTED RHODIUM CATALYSTS IN A CONTINUOUS GAS FLOW REACTOR.....	80
Introduction.....	80
Experimental.....	87
Results and Discussion.....	91
V SUMMARY.....	115
APPENDIX	
COMPUTER PROGRAM.....	117
REFERENCES.....	130
BIOGRAPHICAL SKETCH.....	137

LIST OF TABLES

<u>Table</u>		<u>page</u>
2-1.	Permeation data for PS/[P]-CoSDPT (16.4%) membrane.....	22
2-2.	Separation data for a series of polystyrene blank membranes.....	27
2-3.	Separation data for a series of nickel blank membranes.....	28
2-4.	Difference in oxygen partial pressure for a series of PS/[P]-CoSDPT membranes.....	32
2-5.	Difference in oxygen partial pressure for a series of PS/[P]-CoBr ₂ SDPT membranes.....	33
2-6.	Difference in oxygen partial pressure for a series of PS/[P]-Co3FSDPT membranes.....	34
2-7.	Difference in oxygen partial pressure for a series of PS/[SG]-CoSDPT membranes.....	35
2-8.	Comparison of the difference in oxygen partial pressures obtained with increased cobalt loading in PS/[P]-CoSDPT.....	38
3-1.	Hydroformylation of propylene with RhH(CO)(PPh ₃) ₃	66
3-2.	Oxidation of 1-butene.....	67
3-3.	Butyl sulfide membrane conversion data for various ruthenium catalyzed oxidations by O ₂ at 1 atm. and 90°C.....	71
3-4.	Butyl sulfide membrane turnover data.....	72
3-5.	Butyl sulfide solution reaction conversion data for various ruthenium catalyzed oxidations by O ₂ at 90°C.....	74
3-6.	Hydrogen peroxide formation.....	78

4-1.	Temperature effect upon propylene hydroformylation activity using RhH\SG.....	94
4-2.	Selectivity as a function of time in the hydroformylation of propylene with RhH\SG.....	96
4-3.	Effect of gas flow on the hydroformylation of propylene with RhH\SG.....	100
4-4.	Effect of gas pressure on the hydroformylation of propylene with RhH\SG.....	103
4-5.	Effect of gas ratios on the hydroformylation of propylene with RhH\SG.....	105
4-6.	Catalyst comparison at 80°C.....	109
4-7.	Catalyst comparison at 100°C.....	112

LIST OF FIGURES

<u>Figure</u>		<u>page</u>
2-1.	Molecular orbital diagram. a) Dioxygen; b) Dioxygen adduct of cobalt(II)..	7
2-2.	Polystyrene supported N,N'-bis(salicylidene-imino)di-n-propylamine cobalt(II), [P]-CoSDPT..	10
2-3.	Schematic representation of the dual mode sorption concept.....	13
2-4.	[P]-CoSDPT reaction scheme.....	19
2-5.	Schematic diagram of the gas permeation experimental set up.....	20
2-6.	Plot of the natural log of oxygen partial pressure differential as a function of time for a PS/[P]-CoSDPT, (16.4%), membrane.....	24
2-7.	Plot of the natural log of nitrogen partial pressure differential as a function of time for a PS/[P]-CoSDPT, (16.4%), membrane.....	25
2-8.	Oxygen partial pressure as a function of time. a) Experimental curve. b) Calculated non-facilitated curve. c) Calculated reference curve ($\alpha = 1.00$).....	30
2-9.	Contributions to permeation mechanism.....	40
2-10.	Schematic representation of a metal facilitated transport mechanism due to site to site interaction.....	41
3-1.	Read and Dudley mechanism for the oxidation of terminal alkenes with $\text{RhH}(\text{CO})(\text{PPh}_3)_3$	49
3-2.	Proposed mechanism for the oxidation of terminal alkenes using a rhodium(III)/copper(II) co-catalyst.....	51

3-3.	Alternative mechanism for the oxidation of terminal alkenes using a rhodium(III)/copper(II) co-catalyst.....	52
3-4.	Sulfide oxidation catalysts: a) $[\text{Ru}(\text{O})_2(\text{dmp})_2](\text{PF}_6)_2$ and b) $[\text{Ru}_3\text{O}(\text{prop})_6(\text{H}_2\text{O})_3]^+$	55
3-5.	Anthraquinone autoxidation process.....	56
3-6.	Reactor membrane apparatus.....	61
3-7.	Hydrogen peroxide membrane reactor.....	76
4-1.	Associative and dissociative hydroformylation reaction mechanism.....	84
4-2.	Gas flow reactor schematic.....	90
4-3.	n-Butanal activity as a function of temperature in the hydroformylation of propylene with RhH\SG.....	95
4-4.	Comparison of hydroformylation activity in the production of n-butanal and isobutanal with RhH\SG.....	97
4-5.	Effect of gas flow on the n-butanal activity in the hydroformylation of propylene with RhH\SG..	99
4-6.	Effect of gas pressure on the n-butanal activity in the hydroformylation of propylene with RhH\SG.....	102
4-7.	Effect of gas ratios on the n-butanal activity in the hydroformylation of propylene with RhH\SG.....	104
4-8.	n-Butanal activity for RhH\SG and Rh(tfa)\SG...	107
4-9.	Butanal activity as a function of time in the hydroformylation of propylene with RhH\SG\PC at 100°C.....	113

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

CHEMICAL PROCESSES IN VISCOUS MATERIALS

By

Mark Jay Barnes

August 1989

Chairman: Russell S. Drago
Major Department: Chemistry

Polymer membranes, in which transition metal complexes have been dispersed, have been used to facilitate both oxygen enrichment of air and traditional homogeneous catalytic reactions. The former is a demonstration of facilitated transport of oxygen through a glassy polymer. The latter includes the demonstration of a wide variety of reactions within the polymer environment.

Selective gas permeation through a polymer membrane has become an attractive alternative for conventional gas separation processes. The incorporation of additives that modify permeation properties has been the focus of this research effort in an attempt to enhance the separation ability of the polymer membranes. This effort involves the use of metal complexes to facilitate the transport of gases in a polymer membrane. Specifically, the main objectives investigated were the incorporation of supported cobalt (II) schiff base complexes into polystyrene membranes and the demonstration of metal promoted

enhancement of oxygen permeation in the separation of air. Back calculation using a nickel blank to provide an average separation factor allows for the determination of metal promoted enrichment using the nitrogen permeability coefficient as an internal standard. These results are presented and a transport mechanism discussed.

The use of a polymer environment as the medium for chemical reactions has resulted in a novel approach to heterogenizing homogeneous catalytic reactions. The feasibility of this process has been demonstrated by the hydroformylation of propylene and the oxidation of terminal alkenes. A specific application of the process involves the use of ruthenium catalysts dispersed in composite polymer membranes for the oxidative decomposition of butyl sulfide, a mustard agent simulant. The formation of hydrogen peroxide using the anthraquinone autoxidation process is another application which has been achieved. Results from the above mentioned reactions are presented and discussed.

The development of solid supported rhodium catalysts for heterogeneous hydroformylation reactions has resulted in the production of straight chain aldehydes with high selectivity. Use of these catalysts in a pressure-gas flow reactor is demonstrated and discussed.

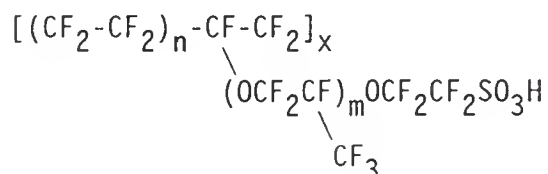
CHAPTER I GENERAL INTRODUCTION

Historically, applications of polymer membrane technology have been dominated by separation processes. The two biggest contributors to this field are reverse osmosis desalination processes and industrial gas separations. Many smaller scale applications which utilize membrane technology are currently being investigated.^{1,2} Drug production and delivery, fermentation, basic chemicals synthesis, hydrogenations and dehydrogenations represent only a portion of these applications. The types of membranes employed are as widely varied as their applications. Ceramic, metallic, glass, inorganic, and polymeric membranes have been used as process media.³⁻⁶ Also of interest is the engineering design in which they are used. Integrated or "hybrid" processes are being developed which combine a membrane separation unit with an existing separation process such as cryogenic separation.^{7,8} Layering or combining the different membrane types may provide systems which allow chemical reaction and product-reactant separation within the same unit.

The work presented in this dissertation is associated with combining membrane technology and transition metal reaction chemistry. The use of polymers and catalysts in conjunction has previously been widely investigated in an attempt to heterogenize known homogeneous catalysts.⁹⁻¹² For the most part, the polymer is used as a support to which the catalyst is covalently attached. These insoluble

functionalized catalysts are then used under "normal" solution chemistry conditions. Alternatively, membrane reactors are systems in which the polymer is used as the medium for reaction. The polymer functions, in essence, as the solvent for the reaction.

The concept of membrane reactors is relatively new. Wolynic and co-workers first published work in this area which dealt with a catalytic liquid membrane reactor used for the production of acetaldehyde from ethylene and oxygen.^{13,14} Since that time most membrane reactor work has been concentrated in two areas. Membrane bioreactors have been shown to be effective in enzyme catalysis^{2,15-17} and porous ceramic and glass membranes have been used as inorganic membrane reactors.³⁻⁶ In the latter case, hydrogenation and dehydrogenation reactions are the main processes being attempted. Catalysis with nafion membranes has also been reported.^{18,19} Nafion possesses a chemically resistant, perfluorinated, polymeric backbone with highly acidic sulfonic acid groups. Its general structure is shown below. It has been used as a super acid catalyst, catalyst support, electrocatalyst, and a gas diffusion membrane.



Even though a considerable amount of work has been conducted in the area of membrane reactors, little of it has actually been achieved

with the use of organic polymers. The work presented here is an attempt at filling this void. Specifically, this study involves three areas of membrane chemistry. The first process investigates the ability of a transition metal complex to affect the permeation properties of a polymeric membrane. The second is concerned with how transition metal complex reactivities are influenced by dispersion in an organic polymer "solvent" environment. The last area examined deals with dispersing transition metal complexes in a non-volatile viscous material which is coated on an inorganic oxide support for the purpose of creating a heterogeneous gas phase reaction process.

CHAPTER II COBALT(II)-FACILITATED TRANSPORT OF DIOXYGEN IN A POLYSTYRENE MEMBRANE

Introduction

The separation of air into its primary components, oxygen and nitrogen, is of major industrial significance. Today, two main commercial processes are used to achieve separation, cryogenic fractional distillation of air²⁰⁻²² and pressure swing adsorption.²³⁻²⁵ Both processes have been employed extensively in the last century for the production of high purity oxygen and nitrogen.

Many applications, however, do not require high purity oxygen but can instead use oxygen enriched air. This market includes waste water treatment facilities, the pulp and paper industry, fermentation processes and numerous medical applications to name a few. Selective gas permeation²⁵⁻²⁸ through a polymer membrane provides an alternative separation method which is becoming increasingly more important in the production of oxygen enriched air.^{29,30}

The past ten years have seen the advent of membrane based separation units. The first commercial venture into the field was initiated by the Monsanto Corporation. It utilized a polysulfone hollow fiber membrane system and was called "The Prism Process."²⁹ Since that time many types of membranes have been increasingly employed for separation purposes, and recently, are being used in conjunction with

the traditional air separation processes.^{31,32} These hybrid systems have been shown to be an economically attractive alternative in the production of pure oxygen and nitrogen. The fact that membrane separation units are economically competitive with existing processes, coupled with the unlimited number of applications, has resulted in an explosion in the amount of research being carried out in this field. Interest is mainly twofold. Most attention is focused on finding new applications for membrane separation units and developing new, or modifying existing, polymers for these applications. The use of membranes for gas separations is based upon the phenomenon that different permeates will have varying rates of permeation through membranes. One of the first references to a membrane separation procedure is credited to Thomas Graham,³³ who, in 1864, used a dialyzer to separate a solution into its components. He became known as the father of gas separations when he published his famous paper "On the Molecular Mobility of Gases"³⁴ in 1863, which resulted in the formulation of Graham's Law, and later published a paper dealing with the separation of gases.³⁵ Since that time many others have made considerable contributions in the areas of membrane chemistry and gas separations, but because of the size and scope of this work, it will not be mentioned in this chapter. Alternately, a more detailed insight into the properties which affect membrane permeation will be presented.

Ideally, a permselective polymer membrane should have good mechanical strength, high selectivity, and high flux (rate of gas permeation). However, the later two are inversely related. A polymer membrane which has a high selectivity will have a relatively slow flux

and vice versa. Attempts to either increase the rate of permeation in highly selective membranes or enhance the selectivity of highly permeable membranes have been the focal point of most research efforts. The work presented in this chapter represents an undertaking in the latter area of modification.

The incorporation of additives to modify permeation properties has been directed towards improving membranes that are highly permeable and poorly selective. A recent approach to this concept involved enhancing the transport of dioxygen by encapsulating a metal complex-containing solution in a porous polymer membrane resulting in excellent selectivity.³⁶⁻³⁹ This liquid-membrane, oxygen-enrichment process utilizes cobalt(II) chelate complexes. The role of the cobalt complex is to act as a carrier by reversibly binding dioxygen and thus increase the oxygen permeability of the membrane. In systems such as these, the most important aspects to be considered are the processes which occur at the carrier site. Essentially, these processes are attributed to the reversible binding ability of the cobalt(II) complex and can be explained by extrapolating our knowledge of similar processes which occur with cobalt(II) complexes in solution.

The ability of the metal center to bind dioxygen and the factors which affect the interaction between the two can be complex. As shown in figure 2-1a, molecular oxygen in its ground state is a triplet, $^3\Sigma_g^-$ molecule with two unpaired electrons residing in the π^* molecular orbitals. Since it is kinetically unfavorable for one of the electrons to change spin, dioxygen is typically unreactive towards diamagnetic compounds. Its ability to bind with transition metal complexes results

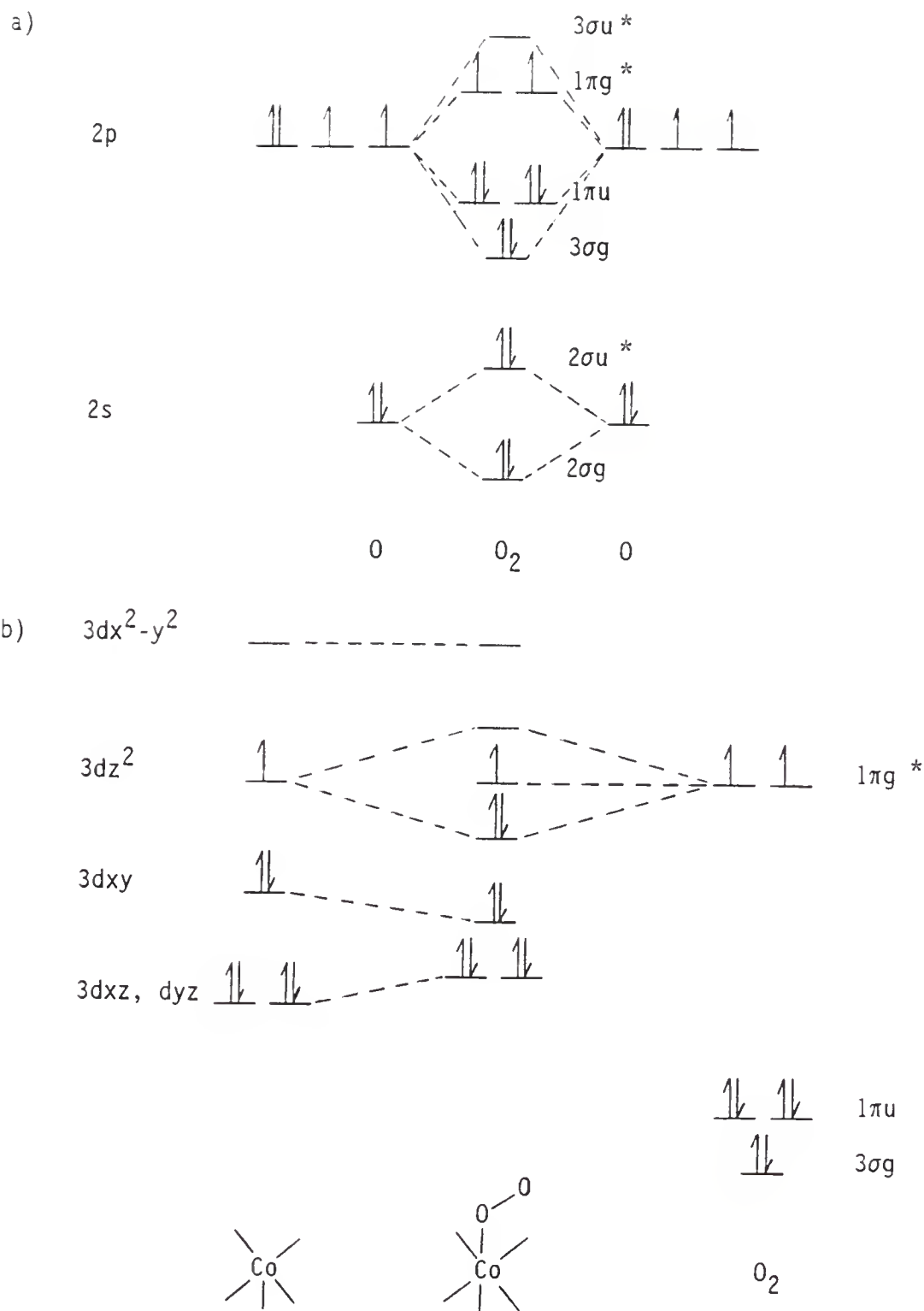


Figure 2-1.

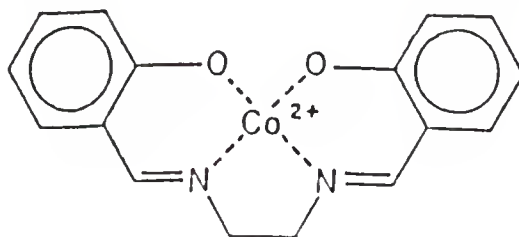
Molecular orbital diagram.

a) Dioxygen; b) Dioxygen adduct of cobalt(II).

primarily from spin orbital coupling, which lessens the severity of a spin change. The spin pairing model⁴⁰ developed by Drago and Corden describes this metal-dioxygen bonding scheme and is shown in figure 2-1b using a simplified molecular orbital diagram. It involves the pairing of the unpaired d_z^2 electron of cobalt(II) with an unpaired π^* electron of dioxygen which results in the formation of an end on bonded cobalt(II)-dioxygen adduct.

The stability of the cobalt-oxygen sigma bond is directly related to the ligand field strength of the complex. By increasing the ligand field strength around the cobalt metal center, the energy of the d_z^2 orbital used in bond formation is increased. Therefore during dioxygen adduct formation, more energy is given off resulting in a more stable cobalt-oxygen sigma bond. This is a critical property since if the bond formed is too stable, the ability to dissociate the dioxygen adduct is hindered. If the bond formed is too weak, the complex will have poor oxygen affinity. Thus a compromise is required to have a suitable carrier.

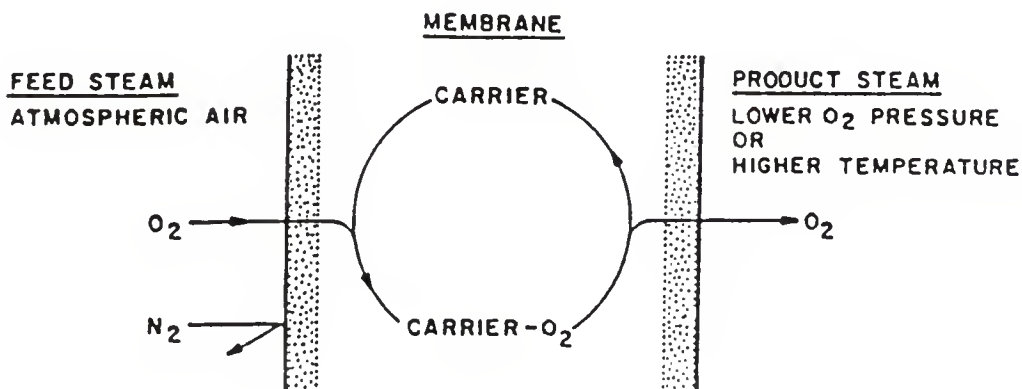
In 1938, Tsumaki reported the first synthetic complex capable of reversibly binding dioxygen, N,N'-bis(salicylidene)ethylenediamine cobalt(II).⁴¹ This complex, better known as cobalt(II) salen, is shown below. Since that time, many cobalt(II) schiff base complexes have been



reported which are capable of reversibly binding dioxygen.

Unfortunately, deactivation of the metal complexes has hindered their development. Deactivation, for the most part, is brought about by either oxidation of the ligand system or irreversible oxidation of the metal center. An example of the latter would be the formation of a μ -peroxodimer complex. Attempts to achieve a stable oxygen carrier have been directed using two different approaches. Sterically constrained metal carrier complexes and supported metal carrier complexes have received the greatest attention. Often, schiff base complexes which indicate promise as carriers are the focus of such modification. This is the case in the work presented in this chapter.

One of the best examples cited which has the ability to bind dioxygen reversibly is N,N'-bis(salicylideneimino)di-n-propylamine cobalt(II), CoSDPT (figure 2-2 with P replaced by H), in 1:1 DMSO and α -butyrolactone solvent encapsulated in a 130 μ thick microporous nylon 6,6 membrane.⁴² At 25°C, an air mixture containing 88% oxygen was produced in a single pass through this membrane. A schematic diagram of this system is illustrated below. Although the process appears quite



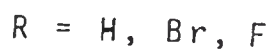
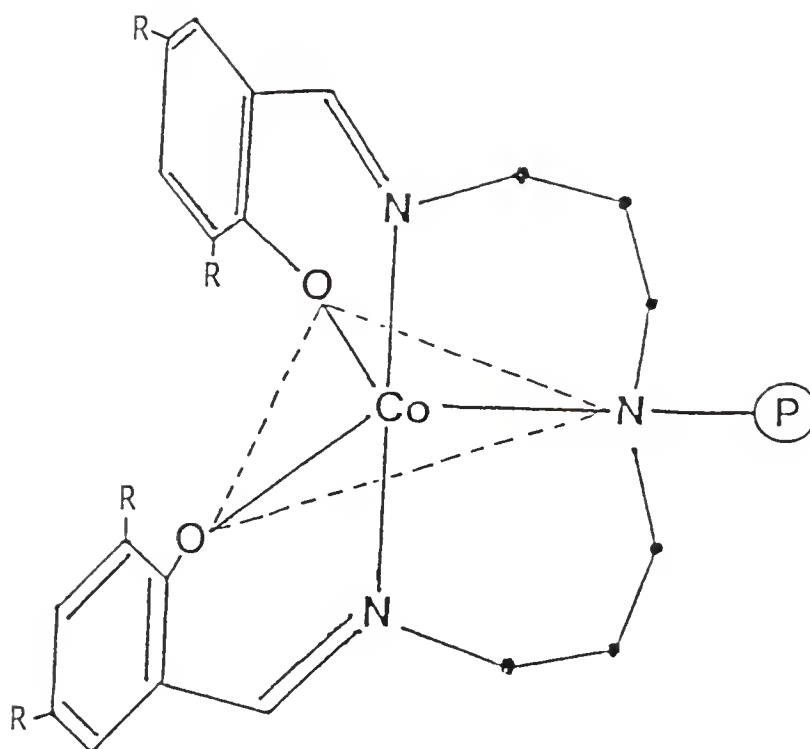


Figure 2-2. Polystyrene supported N,N'-bis(salicylideneimino)di-n-propylamine cobalt(II), [P]-CoSDPT.

remarkable, the removal of the volatile solvent by gas flow has hindered its commercial development. The work presented in this text illustrates the ability to reversibly bind and facilitate the transport of dioxygen through a polymer membrane using this complex supported on polystyrene. A few reports of facilitated transport of dioxygen by carriers in membranes have appeared^{43,44} using unsupported complexes that can be viewed as being dissolved in the polymer.

The concept of a facilitated transport mechanism has been a controversial subject in membrane separations. Therefore, a brief mathematical description of permeation in a polymer membrane is necessary. According to Fick's Law of diffusion, shown below, the flux,

$$J = DS\Delta P/l$$

J , of a penetrant can be determined from its diffusion coefficient, D ; solubility, S ; and pressure differential, P , across a membrane of thickness l . The permeability of the gas, $\bar{P}$, is dependent upon both its solubility and diffusivity in the respective membrane.

$$\bar{P} = DS$$

Generally, sorption and transport in a glassy polymer such as polystyrene is best explained by a dual mode model. Using this model, two simultaneous processes in the membrane are predicted to occur. The first is associated with dissolution in the dense region of the polymer and follows Henry's Law where C_D is the concentration, K_D is the Henry's

$$C_D = K_D P$$

law constant which characterizes sorption of the penetrant, and P is the pressure of the penetrant. The second process is associated with distribution in the gaps or "holes" of the polymer and is best explained by a Langmuir isotherm where C_H is the concentration, C_H' the Langmuir

$$C_H = C_H' B P / (1 + B P)$$

sorption capacity, and B the affinity of the penetrant for the gaps in the polymer. Using these simple equations, the total concentration of the penetrant can be described as the sum of the two individual

$$C = C_D + C_H$$

concentrations. This can be seen schematically in the concentration versus pressure graph shown in figure 2-3. The overall solubility isotherm can similarly be described as the sum of the solubility expressions of each model. The permeability of the penetrant

$$S = K_D + C_H' B / (1 + B P)$$

can now be expressed as the diffusivity and solubility associated with each individual mode where D_D and D_H represent the diffusivities of the Henry's mode and Langmuir mode respectively.

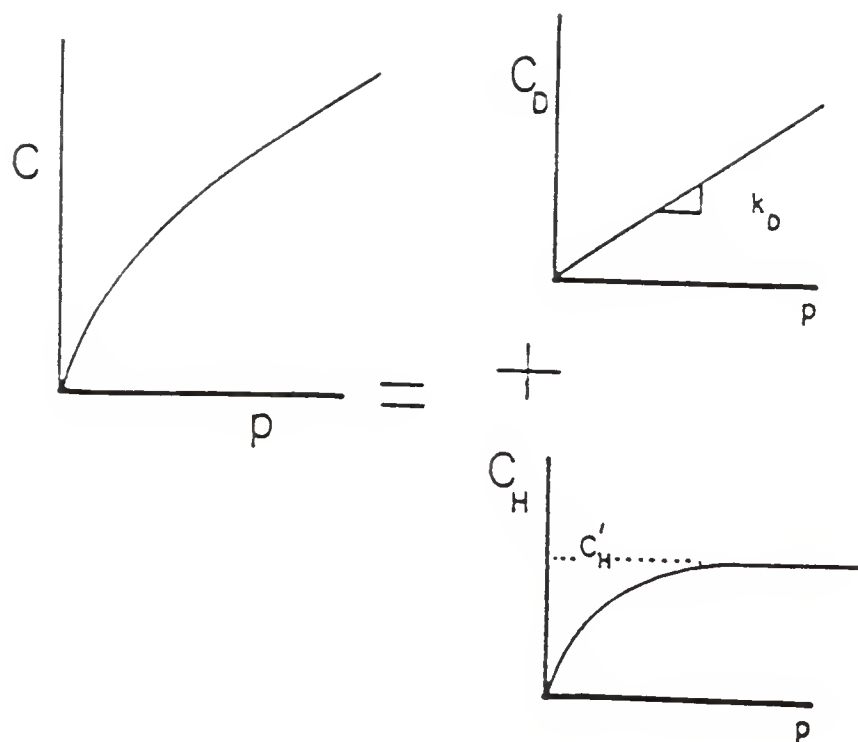


Figure 2-3. Schematic representation of the dual mode sorption concept.

$$\bar{P} = K_D D_D + C_H' B D_H / (1 + B P)$$

The model presented is representative of a nonfacilitated process and must therefore be modified to explain the contributions made by a facilitated transport mode. This can be done by initially applying Langmuir kinetics to describe the equilibrium obtained when oxygen binds to solid metal complexes. The resulting expression can then be rearranged to indicate the fraction of oxygenated sites, X , with

$$X / (1 - X) = K P_{O_2}$$

$$X = K P_{O_2} / (1 + K P_{O_2})$$

respect to the equilibrium constant, K , and dioxygen partial pressure. The fraction of oxygenated sites should be directly related to the solubility of dioxygen associated with these sites. Therefore, a new solubility isotherm may be written to express the total solubility of dioxygen in a membrane capable of facilitating dioxygen transport. Similarly, a new expression describing dioxygen permeability according to the three modes of transport can be formulated where D_M represents the diffusivity associated with the metal sites.

$$S = K_D + [C_H' B / (1 + B P)] + [K P / (1 + K P)]$$

$$\bar{P} = K_D D_D + [C_H' B D_H / (1 + B P)] + [K P D_M / (1 + K P)]$$

The results presented in this work represent a new approach to enhancing the permeation properties of polymer membranes and establishing a novel method and mechanism of transport. The goal of this research was to demonstrate this novel mode of transport as well as to develop a process that accurately accounted for the quantities of dioxygen associated with both facilitated and nonfacilitated transport. To achieve this, a metal complex that reversibly binds dioxygen is covalently attached to polystyrene. Though the pure complexes in the solid state do not bind dioxygen, they do bind dioxygen in the solid state when covalently linked to a polymer.⁴⁵ The dispersion of the metal complex on highly crosslinked polystyrene into a polystyrene film resulted in the selective permeation of dioxygen through the membrane. This membrane system differs from the liquid membranes in that the metal complexes are bound to the polymer. Since the cobalt complexes are not mobile, the mechanism is unlike that proposed for isotropic polymers or liquid membranes as demonstrated in the Bend Research system.⁴²

Recently, this system has been extended to cobalt(II) porphyrin and Schiff base complexes.⁴⁶⁻⁴⁹ In all reports^{43,44,46-51} of facilitated transport in solid polymer membranes, the demonstration of facilitated transport by metal complex binding of dioxygen is dependent upon the critical selection of a blank. Incorporation of a material in a polymer film can function to change the structure of the membrane and the permeability of gases leading to enrichment by a process other than facilitated transport. The results of this study are significant for they provide strong support for a facilitated transfer mechanism using metal complexes to bind simple gas molecules. A procedure for the

evaluation of the experimental permeation data is reported that eliminates imperfections including solvent entrapment that surely exist in the test and blank films.

Experimental

Complexes studied were prepared using reagents which were either purchased or synthesized using the procedures listed below. An overall reaction scheme is shown in figure 2-4 for the preparation of the polystyrene supported complexes. Solvents used in this work were purified by distillation, stored over 4A molecular sieves under a nitrogen atmosphere, and degassed prior to use when necessary. Characterization of the complexes was conducted using a Perkin Elmer Plasma II Emission Spectrometer, and Bruker ER 200D-SRC Electron Spin Resonance Spectrometer. Elemental analyses were conducted by the University of Florida Department of Chemistry Microanalysis Service, and Galbraith Laboratories.

Polystyrene Supported Dipropyleneetriamine, [P]-DPT

Polystyrene beads (90% chloromethylated, 4% divinylbenzene crosslinked) were donated by Sybron Corporation. Polystyrene bound dipropyleneetriamine was prepared according to the literature.⁴⁵ Experimental analysis: %C = 67.41, %H = 6.64, %N = 7.60. Theoretical analysis: %C = 72.83, %H = 10.19, %N = 16.98.

Polystyrene Supported Bis(3-(salicylideneamino)propyl)amine, [P]-SDPT

The polymer bound pentadentate ligand was prepared according to the literature.⁴⁵ The 3,5-dibromo and the 3-fluoro substituted

salicylaldehyde derivatives were prepared in a similar manner.

Experimental analysis: %C = 75.97, %H = 7.19, %N = 7.84. Theoretical analysis: %C = 76.45, %H = 7.30, %N = 9.22.

[P]-CoSDPT, -Co Br₂SDPT and -Co3FSDPT

Cobalt was incorporated into the [P]-SDPT type complexes by slurrying excess cobalt(II) acetate with the appropriate resins in DMF under argon at room temperature for two days. The polymer supported cobalt complexes were filtered, washed with DMF and dried under vacuum at 80°C. Experimental analysis of [P]-CoSDPT: %Co = 0.15. Theoretical analysis: %Co = 11.50. Overall analysis indicated greater than 95% of the chloromethylated polystyrene had been converted to the [P]-SDPT and that 1.15% of the SDPT ligand contained cobalt. The low loading of cobalt was ideal for this study because site isolation inhibits formation of the μ -peroxo dimer. EPR studies showed an intense cobalt-dioxygen signal which was used to monitor reversible binding of O₂.

Silica Gel Supported CoSDPT, -CoBr₂SDPT and -Co3FSDPT

Silica gel supported dipropylenetriamine was prepared as reported in the literature.⁵² The silica supported Cobalt(II)SDPT complexes were prepared from [SG]-DPT in an analogous manner to the polystyrene bound analogues. Experimental analyses were not obtained.

[P]-NiSDPT, -NiBr₂SDPT, and [SG]-NiSDPT

The analogous nickel complexes were prepared in the same manner as reported for the cobalt complexes. Analyses were not obtained.

Membrane Preparation and Characterization

The membranes employed in this study were prepared using a casting technique. Polystyrene was dissolved in an appropriate solvent, such as

toluene or methylene chloride. The viscous polymer solution was then poured into a leveled circular form. Evaporation of solvent at room temperature resulted in the formation of homogeneous polymer membranes.

Membranes containing the supported metal complexes were prepared in a similar manner by grinding the complex into a fine powder ($< 1\mu$ in diameter), adding it to the polymer solution, and then casting the solution in a mold. After solvent evaporation had occurred, the membrane's thickness was determined with a vernier caliper to the nearest hundredth of a millimeter. The weight percent of the added complex in the membrane was determined after each permeation experiment by redissolving the polymer film, isolating and drying the supported complex and then weighing it.

Permeation Apparatus

Permeation experiments were carried out with an apparatus designed by Ken Balkus.⁵⁰ The cell was designed to support the membrane and prevent rupturing when a pressure gradient was applied to the membrane. A schematic of the permeation setup is shown in figure 2-5.

Permeation Procedure

The following section describes a typical experimental permeation procedure. A polymer membrane was secured between the two chambers of the apparatus, after which the membrane deformed to the shape of the o-rings used to secure its seal. The lower chamber of the cell was placed under vacuum for approximately six to twelve hours prior to the start of the experiment to remove any excess solvent or O_2 that may have been trapped in the film during preparation. The lower chamber was then closed off under vacuum and an initial pressure measurement taken.

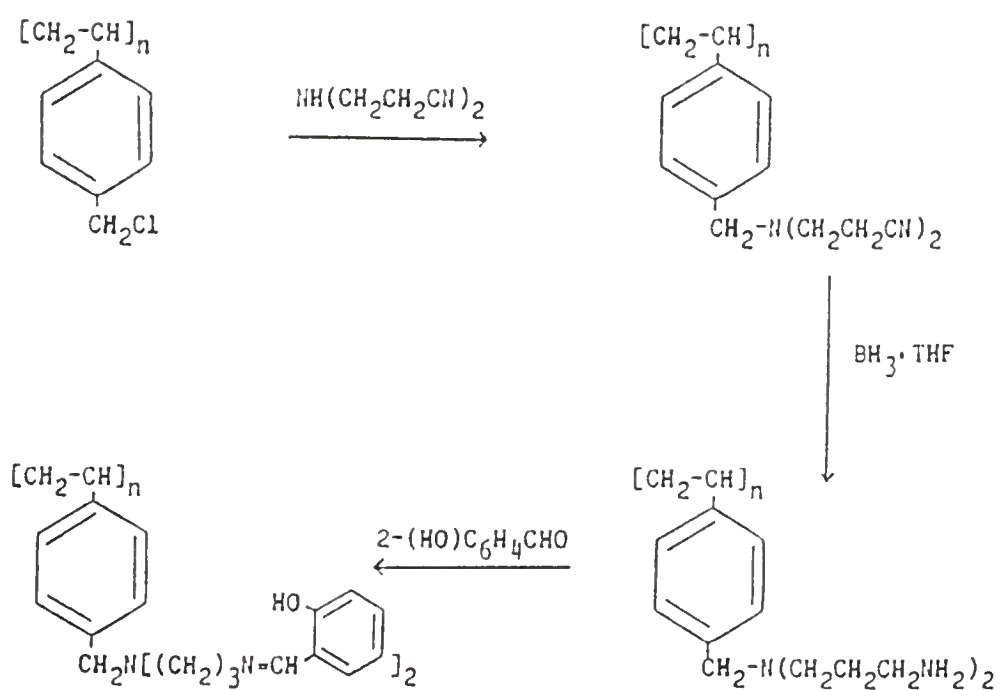


Figure 2-4. [P]-CoSDPT reaction scheme.

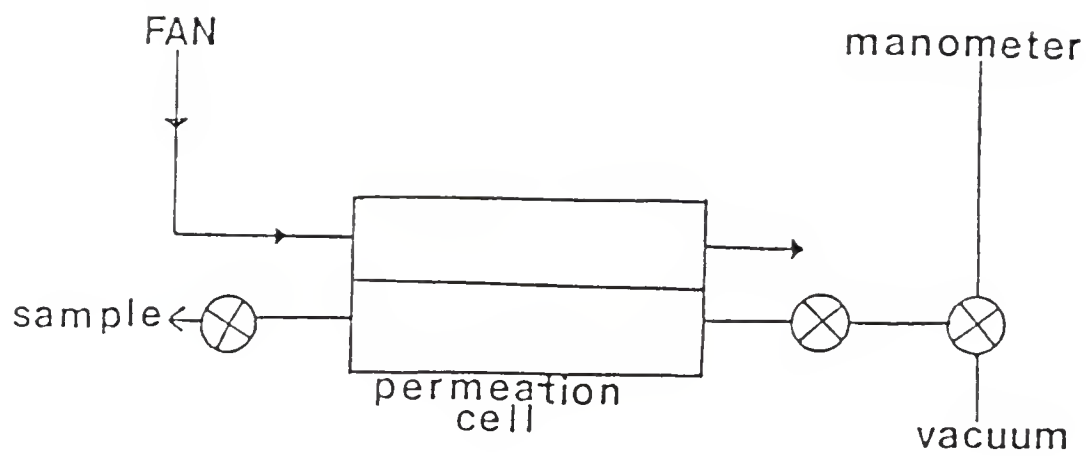


Figure 2-5. Schematic diagram of the gas permeation experimental set up.

Periodically, the lower chamber was monitored manometrically to determine the extent of gas permeation and quantitatively to determine its dioxygen (also referred to as oxygen) content. The latter analysis was carried out using gas samples taken from the lower chamber with a 100 μ l gas tight syringe and analyzed by a Varian 3700 gas chromatograph equipped with a thermal conductivity detector. The column employed was an 8 foot, 1/8 inch O.D., stainless steel column containing 5A molecular sieves heated to 30°C.

Since the gas sample taken was at a reduced pressure, it was diluted with air while being withdrawn from the sampling port. From the percent oxygen of the injected sample determined by the GC, the actual percent oxygen in the lower chamber was calculated using the equation shown below, where P_L is the pressure of the lower chamber in mmHg, P_H

$$(P_L)(O_L) + (P_H - P_L)(O_H) = (P_H)(O_D)$$

is atmospheric pressure, O_L is the percent oxygen in the lower chamber, O_H is the percent oxygen in the atmosphere, and O_D is the percent oxygen as determined by the GC. Using this method, the standard deviation between samples was typically on the order of 0.1%.

Results and Discussion

The evaluation of the cobalt containing membranes is based upon a comparison of experimental permeation data with data obtained from an appropriate blank. Permeation data for a typical PS/[P]-CoSDPT membrane

are shown in table 2-1. The percent oxygen was calculated as previously described and the percent enrichment is the difference between the percentage of oxygen in the lower chamber and that of air, which is assumed to be 21.0%.

Table 2-1. Permeation data for PS/[P]-CoSDPT (16.4%) membrane.

Time (hr)	Total Pressure (mmHg)	Flux (mmHg/hr)	Partial Pressure		Percent Oxygen	Percent Enrichment
			Oxygen (mmHg)	Nitrogen (mmHg)		
5	36.0	7.20	10.56	25.44	29.3	8.3
18	71.0	3.94	23.77	47.23	33.5	12.5
24	92.0	3.83	29.78	62.22	32.4	11.4
29.5	99.0	3.35	32.97	66.03	33.3	12.3
42	118.0	2.81	40.27	77.73	34.1	13.1

According to Henry's Law, permeation of a gas through a membrane is a first order kinetic process. This is shown mathematically below, where $\bar{P}$ is the permeability coefficient ($\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{s mmHg}$), l is the film thickness (cm), A is the film area (cm^2), V_{cell} is the volume of the lower chamber (cm^3), $(P_H - P_L)$ is the partial pressure differential across the membrane (mmHg), R is the gas constant ($6.24 \times 10^4 \text{ cm}^3\text{mmHg}/\text{molK}$), and T is the temperature (K). Assuming P_H is constant

$$\frac{dP}{dt} = \frac{RTA}{22,414V_{\text{cell}}} \frac{\bar{P}(P_H - P_L)}{l}$$

throughout the experiment, the equation can be rearranged and integrated to give a new equation from which a plot of $\ln(P_H - P_L)$ versus time should yield a straight line, indicating a first order process.

$$\ln(P_H - P_L) = \frac{-RTA}{22,414V_{\text{cell}}} \frac{\bar{P}}{1} t + \text{constant}$$

This analysis was carried out using the computer program detailed in Appendix A. Using this program, the permeability coefficients for both oxygen and nitrogen can be obtained from the slope of the lines plotted from their respective partial pressures in table 2-1. Graphs of these analyses are shown in figures 2-6 and 2-7. Values of 4.38×10^{-10} and $1.92 \times 10^{-10} \text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{s mmHg}$ are obtained respectively. However, in the cobalt complex containing films, it is obvious that a slightly curved line is obtained rather than a linear one. This indicates that the permeability coefficient of oxygen is varying with the partial pressure of oxygen in the lower chamber. Therefore, oxygen permeation through the membrane is deviating from a first order process due to contributions from facilitated transport.

To better demonstrate and quantify the contributions resulting from facilitated transport, the cobalt containing films must be compared to an appropriate blank. Analogous nickel(II) complexes do not bind oxygen, since they have no unpaired electrons, and are similar in structure to the cobalt complexes resulting in membranes with similar morphology and free space volumes. Although free volume is difficult to reproduce in glassy polymers because of air pockets and filler

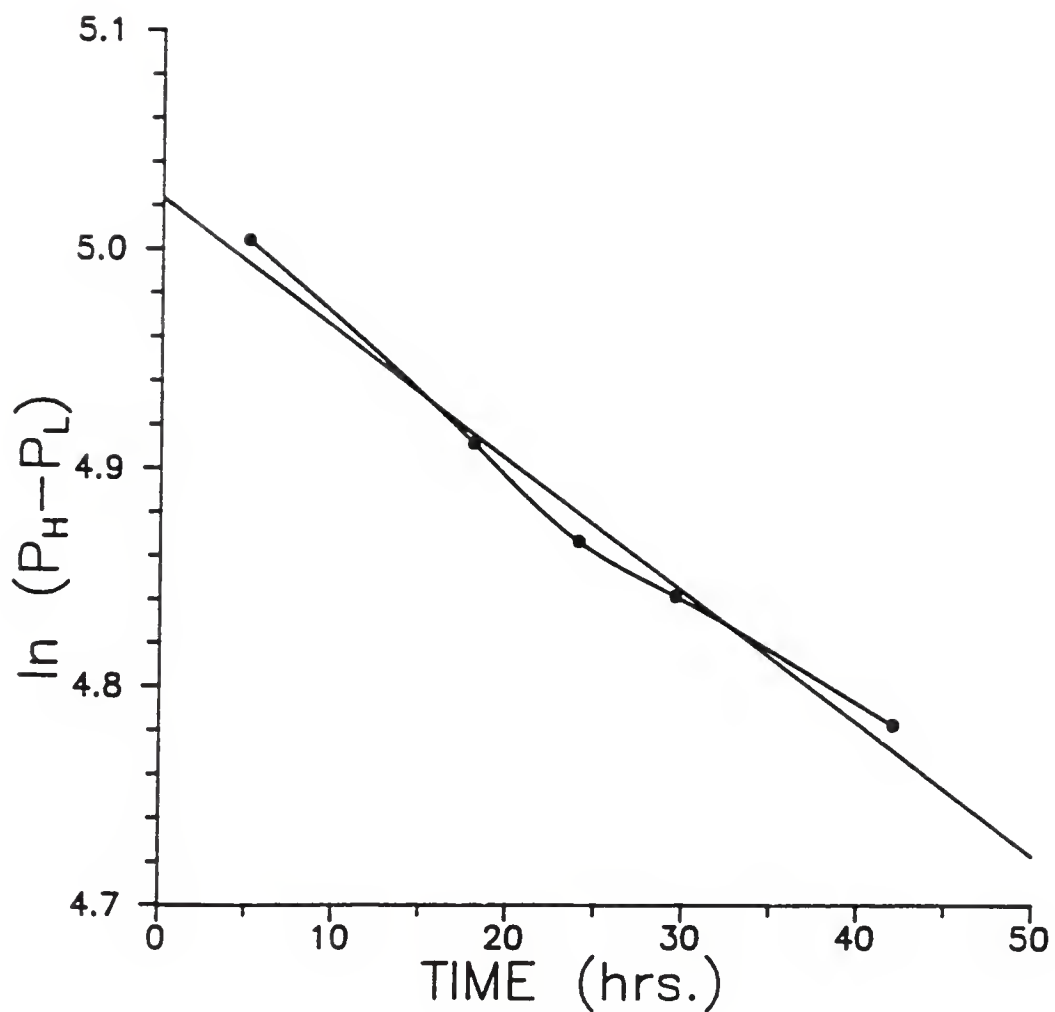


Figure 2-6.

Plot of the natural log of oxygen partial pressure differential as a function of time for a PS/[P]-CoSDPT, (16.4%), membrane.

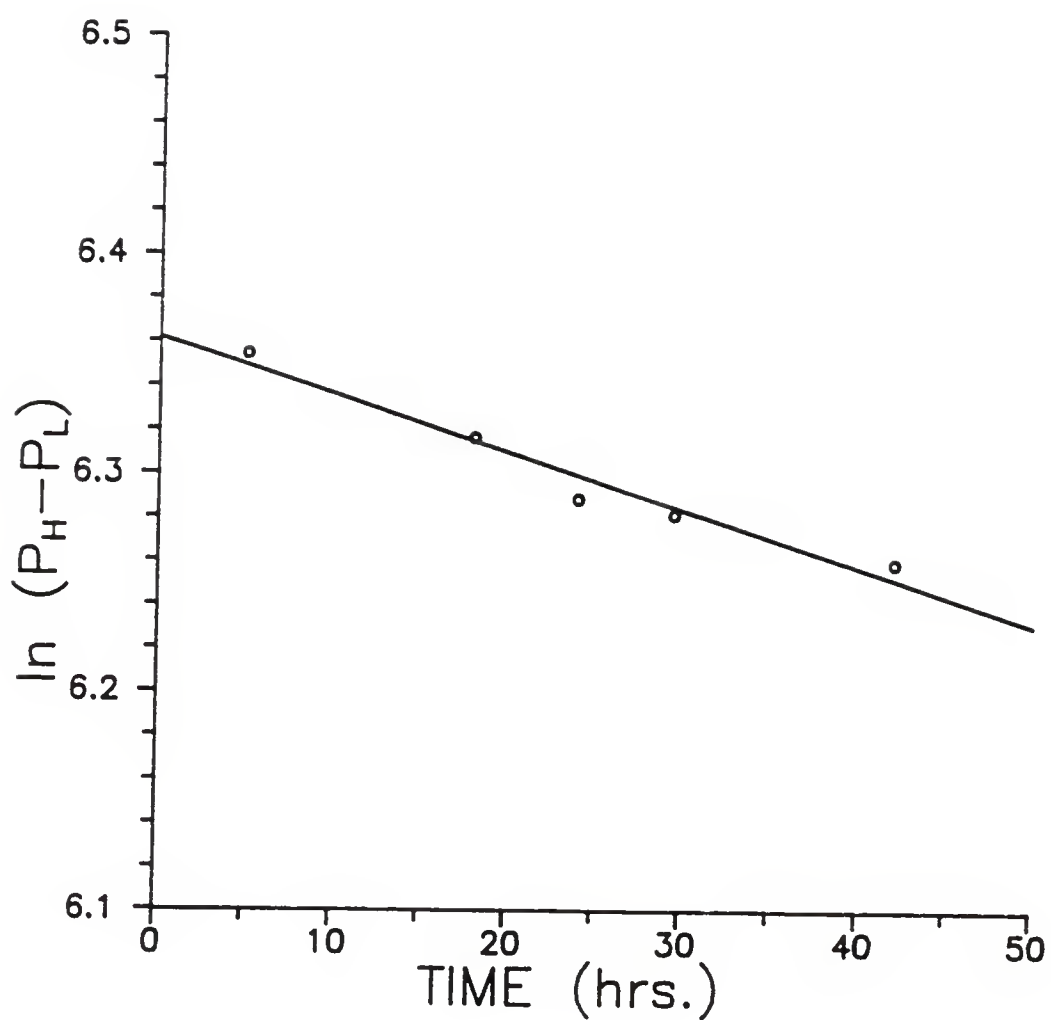


Figure 2-7.

Plot of the natural log of nitrogen partial pressure differential as a function of time for a PS/[P]-CoSDPT, (16.4%), membrane.

aggregation, the nickel complexes are the best simulation for the unoxygenated cobalt containing films and, therefore, are ideal blanks. Analysis of the polystyrene and nickel blanks is best made by observing the ratio of $\bar{P}_{O_2}$ to $\bar{P}_{N_2}$. This value is known as the separation factor, α , and describes the effectiveness of a membrane for permselectivity. The α values for both polystyrene and nickel blank membranes are reported in tables 2-2 and 2-3 respectively.

Certainly, all films contained minor defects, some more severe than others. An extensive amount of data was collected for a large number of films. In several instances pinholes were present in the original film or leaks developed as the experiment progressed. In order for a run to be found acceptable, it was required that the first data point have as an upper limit, a value of flux times length, ($J \times l$), below 7.0 (torr·mm/hr) at the start of the experiment. A second requirement was that in each experiment the flux must decrease as $(P_H - P_L)$ decreases i.e., as time increases. This criterion was used to discard data sets in which leaks developed during the experiment. A series of 11 films of polystyrene selected by these requirements and with varying thicknesses was studied yielding a mean oxygen permeability coefficient of $3.1 \times 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm}/(\text{cm}^2\text{s mmHg})$ with a standard deviation of $\pm 0.8 \times 10^{-10}$. This permeability coefficient is approximately one order of magnitude greater than those previously reported.⁵³⁻⁵⁷ This is not surprising since polystyrene is a glassy polymer and the method of membrane preparation will affect the transport properties of the membrane.^{58,59} Systematic errors introduced by the apparatus or sampling technique may also contribute to the deviation.

Table 2-2. Separation data for a series of polystyrene blank membranes.

l (mm)	Jl (torr•mm/hr)	Pts. ^a	α
$0.371 \pm .073$	1.7	3F	$2.52 \pm .02$
$0.542 \pm .124$	2.3	4M	$1.37 \pm .02$
$0.50 \pm .00$	3.4	6F	$2.14 \pm .02$
$0.164 \pm .05$	4.3	4M	$1.40 \pm .01$
$0.150 \pm .052$	1.5	4M	$1.72 \pm .01$
$0.250 \pm .052$	1.2	5M	$2.19 \pm .04$
$0.110 \pm .028$	1.0	7F	$2.27 \pm .02$
$0.131 \pm .048$	1.9	9F	$2.34 \pm .03$
$0.989 \pm .16$	5.4	5F	$1.97 \pm .05$
$1.567 \pm .30$	4.3	4F	$2.76 \pm .20$
$0.238 \pm .051$	1.5	3M	$1.03 \pm .16$

Avg. $\alpha = 1.97$ S.D. = 0.17

^a number of data points in the data set. E, M, F designate the time span of the experiment where E is less than 12 hrs., M is less than 29 hrs., and F is greater than or equal to 29 hrs.

Table 2-3. Separation data for a series of nickel blank membranes.

<u>[P]-NiSDPT</u>				
<u>1st Cycle</u>				
WT %	l (mm)	Jl (torr•mm/hr)	Pts. ^a	α
20	0.457 $\pm$.119	4.8	4E	1.79 $\pm$.01
15	0.681 $\pm$.059	3.1	5M	2.05 $\pm$.02
10	0.423 $\pm$.103	4.0	5E	1.57 $\pm$.02
Avg. α = 1.80			S.D. = 0.17	
<u>[P]-NiBr2SDPT</u>				
<u>1st Cycle</u>				
20	0.432 $\pm$.12	3.9	5E	2.26 $\pm$.03
20	0.700 $\pm$.168	5.2	5M	1.80 $\pm$.12
15	0.600 $\pm$.160	3.0	6M	1.94 $\pm$.06
10	0.628 $\pm$.138	4.4	5M	1.79 $\pm$.08
Avg. α = 1.95			S.D. = 0.13	
<u>2nd Cycle</u>				
25	0.709 $\pm$.159	3.5	4M	2.12 $\pm$.02
<u>[SG]-NiSDPT</u>				
25	0.694 $\pm$.105	4.5	5M	1.77 $\pm$.05
20	0.666 $\pm$.114	3.0	5M	1.73 $\pm$.01
15	0.730 $\pm$.079	4.7	4M	2.00 $\pm$.04
Avg. α = 1.83			S.D. = 0.10	

^a number of data points in the data set. E, M, F designate the time span of the experiment where E is less than 12 hrs., M is less than 29 hrs., and F is greater than or equal to 29 hrs.

The permeabilities were also determined from a gas mixture rather than a single component gas penetrating through the membrane. The few studies reported with permeations of gas mixtures through glassy polymers show deviations in permeabilities of pure penetrants versus those of the mixture.⁶⁰ Although deviations from the literature values exist, the important point to be considered is that all films were similarly made and evaluated so that consistent data could be obtained and compared.

Using $\bar{P}_{N_2}$ as an internal standard ensures that the cobalt complex-containing membranes can be compared with their respective blanks and the difference in oxygen partial pressures can be attributed to metal promoted enhanced oxygen permeability and not to film preparation or defects. To illustrate the enrichment that is obtained by facilitated transfer, the partial pressure of oxygen in the lower chamber has been plotted as a function of time for PS/[P]-CoSDPT (16.4% functionalized ligand with 0.15% cobalt) membrane (figure 2-8). The change in nitrogen partial pressure with time for this film is used as an internal standard to calibrate the permeation experiment. The average α value from the PS/[P]-NiSDPT blanks is used to calculate the oxygen partial pressure corresponding to this nitrogen pressure for an identical membrane in which facilitated transport does not occur and a first order kinetic process is observed. Since the cobalt complex does not bind nitrogen and facilitate its transport, this affords an ideal blank. This calculated pressure of oxygen is representative of all diffusion mechanisms other than facilitated transport and is also plotted in figure 2-8. The difference between the curves represents the enrichment obtained by a cobalt(II) facilitated transport mechanism. Again this

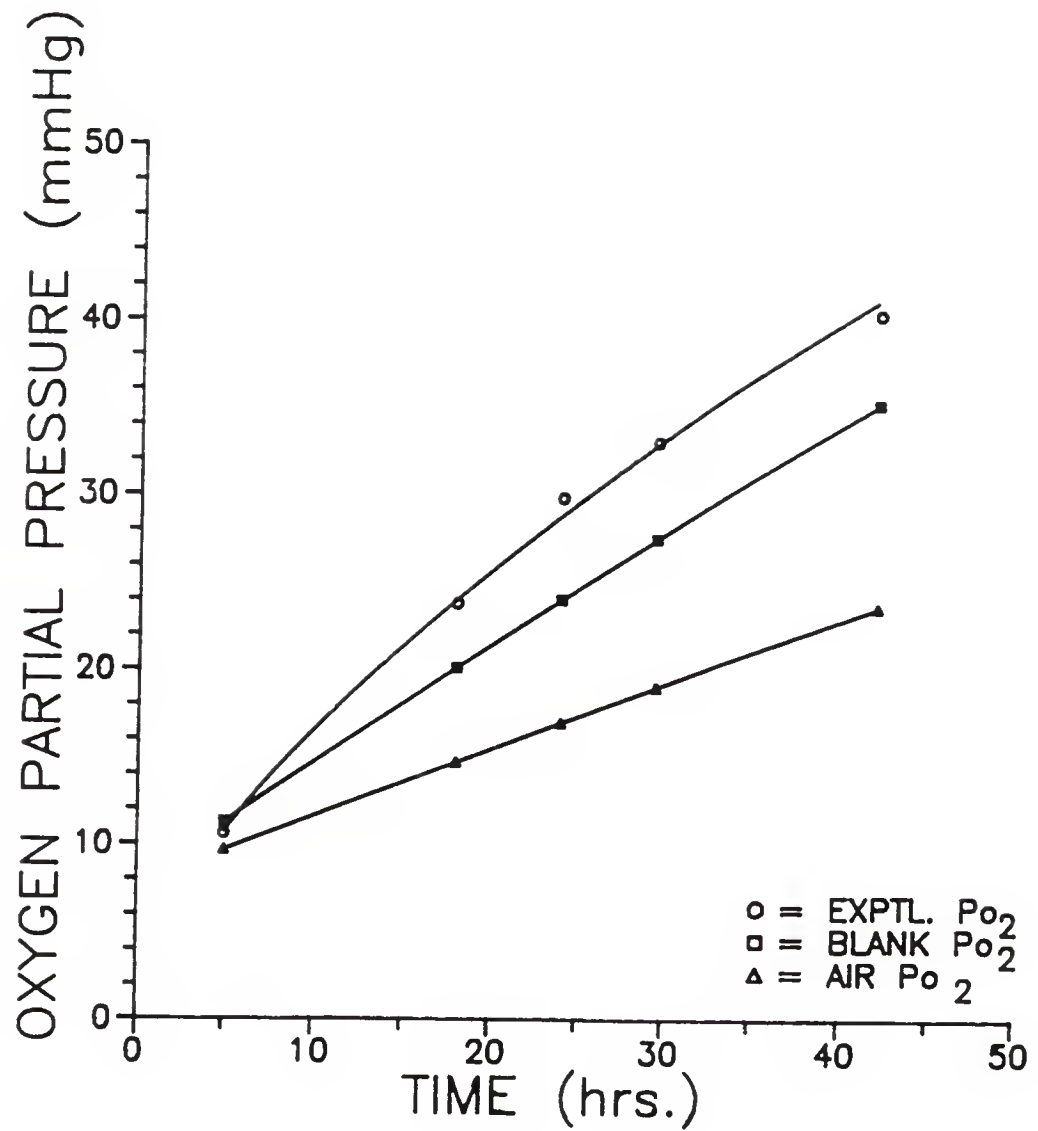


Figure 2-8.

Oxygen partial pressure as a function of time.
 a) Experimental curve. b) Calculated non-facilitated curve. c) Calculated reference curve ($\alpha = 1.00$).

analysis was conducted using the computer program listed in appendix A. Figure 2-8 also contains a reference curve indicating the oxygen partial pressure which would be present if no permselectivity were achieved, i.e. $\alpha = 1.00$.

By analyzing the data using the blank nickel α values and nitrogen permeability coefficients from the cobalt containing membranes, systematic errors in measuring the enrichment of oxygen (such as membrane thickness and imperfections) are cancelled out. This is verified experimentally with the nickel blanks themselves, where α is independent of film thickness. It was also observed in the nickel data, that percent loading and variation in substituents on the phenyl ring did not influence the α values within the experimental standard deviation of ± 0.2 . The reaction chamber can be evacuated after 25 hours and the experiment cycled a second time with no change in α .

Table 2-4 contains the differences in partial pressures of oxygen between the cobalt facilitated and back-calculated non-facilitated curves (as plotted in figure 2-8) for a series of cobalt complex containing membranes. The differences were determined graphically at three different reaction times: when the back-calculated non-facilitated partial pressure of oxygen, $P_{O_2}^B$, was 15, 20, and 25 torr. The polymer bound CoSDPT complex shows an enrichment of oxygen over the non-facilitated process. The increasing oxygen partial pressure at the three different reaction times can be explained by the variance in its permeation coefficient. Early in the experiment, the oxygen permeation coefficient is largest leading to an increase in the difference in P_{O_2} . Later in the experiment, the increased P_{O_2} value in

Table 2-4. Difference in oxygen partial pressure for a series of PS/[P]-CoSDPT membranes.

<u>[P]-CoSDPT</u>					
<u>1st Cycle</u>					
WT%	l (mm)	Jl (torr·mm/hr)	Difference in P_{O_2} (torr)		
			$P_{O_2}^B$ 15	$P_{O_2}^B$ 20	$P_{O_2}^B$ 25
44	0.261 ± .144	2.4	3.7	N.A.	N.A.
18.6	0.357 ± .065	2.6	1.0	2.5	2.6
16.4	0.687 ± .124	4.9	<u>2.3</u>	<u>4.1</u>	<u>4.9</u>
		Avg. $P_{O_2} =$	2.3	3.3	3.8
		S.D. =	1.0	1.1	1.6
<u>2nd Cycle</u>					
17.2	0.677 ± .044	5.1	4.2	5.0	5.9
16.4	0.687 ± .124	2.5	<u>2.8</u>	<u>3.6</u>	<u>4.2</u>
		Avg. $P_{O_2} =$	3.5	4.3	5.0
		S.D. =	1.0	1.0	1.2
<u>3rd Cycle</u>					
16.4	0.687 ± .124	2.9	2.6	3.2	3.6
<u>4th Cycle</u>					
16.4	0.687 ± .124	4.4	-2.4	-3.5	-3.9

Table 2-5.

Difference in oxygen partial pressure for a series of PS/[P]-CoBr₂SDPT membranes.

<u>[P]-CoBr₂SDPT</u>					
<u>1st Cycle</u>					
WT%	l (mm)	Jl (torr·mm/hr)	Difference in P_{O_2} (torr)		
			P_{O_2} 15	P_{O_2} 20	P_{O_2} 25
7.4	0.528 ± .072	3.7	2.9	3.9	4.0
6.76	0.671 ± .047	6.7	<u>2.6</u>	<u>3.5</u>	<u>4.4</u>
		Avg. P_{O_2} =	2.8	3.7	4.2
		S.D. =	0.2	0.3	0.3
<u>2nd Cycle</u>					
20.20	0.640 ± .051	5.8	-5.8	-4.5	-5.6
12.62	0.747 ± .074	3.7	<u>-4.0</u>	<u>N.A.</u>	<u>N.A.</u>
		Avg. P_{O_2} =	-4.9	-4.5	-5.6
		S.D. =	1.3		

Table 2-6. Difference in oxygen partial pressure for a series of PS/[P]-Co3FSDPT membranes.

<u>[P]-Co3FSDPT</u>					
<u>1st Cycle</u>					
WT%	l (mm)	Jl (torr·mm/hr)	Difference in P_{O_2} (torr)		
			$P_{O_2}^B$ 15	$P_{O_2}^B$ 20	$P_{O_2}^B$ 25
24.6	0.359 ± .050	2.3	6.0	7.1	7.9
16.47	0.506 ± .075	4.4	1.0	0.6	0.0
6.42	0.625 ± .085	5.9	3.0	4.0	4.4
6.30	0.541 ± .051	3.8	<u>5.4</u>	<u>5.0</u>	<u>5.0</u>
		Avg. P_{O_2} =	3.8	4.2	4.3
		S.D. =	1.3	1.6	1.9
<u>2nd Cycle</u>					
24.6	0.359 ± .050	1.4	-2.1	N.A.	N.A.
6.30	0.541 ± .051	2.4	<u>0.5</u>	<u>1.0</u>	<u>1.3</u>
		Avg. P_{O_2} =	-0.8	1.0	1.3
		S.D. =	1.8		

Table 2-7.

Difference in oxygen partial pressure for a series of PS/[SG]-CoSDPT membranes.

<u>[SG]-CoSDPT</u>					
<u>1st Cycle</u>					
WT%	l (mm)	Jl (torr•mm/hr)	Difference in P_{O_2} (torr)		
			$P_{O_2}^B$ 15	$P_{O_2}^B$ 20	$P_{O_2}^B$ 25
14.9	$0.533 \pm .097$	5.6	1.0	2.1	2.5
10.0	$0.807 \pm .70$	6.4	2.8	3.0	3.2
6.56	$0.571 \pm .082$	4.8	1.6	1.5	0.9
4.6	$0.614 \pm .077$	6.1	2.6	3.1	3.0
2	$0.492 \pm .028$	4.9	<u>1.3</u>	<u>2.6</u>	<u>2.6</u>
		Avg. $P_{O_2} =$	1.9	2.5	2.4
		S.D. =	0.4	0.3	0.4
<u>2nd Cycle</u>					
16.5	$0.647 \pm .051$	4.2	4.0	N.A.	N.A.
14.9	$0.533 \pm .097$	3.2	2.5	3.2	2.5
10.0	$0.807 \pm .70$	5.6	<u>2.0</u>	<u>2.2</u>	<u>2.5</u>
		Avg. $P_{O_2} =$	2.8	2.7	2.5
		S.D. =	0.7	0.7	0.0
<u>Lower Surface Studies</u>					
16.1	$0.384 \pm .037$	4.6	0.7	0.0	-0.5
1.87	$0.358 \pm .062$	2.7	<u>-1.0</u>	<u>-1.6</u>	<u>-1.5</u>
		Avg. $P_{O_2} =$	-0.2	-0.8	-1.0
		S.D. =	1.2	1.1	0.7

the lower chamber approaches the $P_{1/2}$ value of the complex and the facilitated transport of oxygen decreases. Eventually the cobalt complex is fully oxygenated and does not facilitate oxygen transport. At this point in time, no subsequent enrichment occurs, i.e. the experimental P_{O_2} curve and blank back-calculated curves become parallel (figure 2-8). This is observed in all cases with the different cobalt complexes.

Second and third cycle experiments with PS/[P]-CoSDPT membranes produced similar enrichments in comparison with the original experiment. The fourth cycle showed a loss of enrichment presumably because of formation of a μ -peroxo complex or oxidation of the cobalt(II) complex. While cycling experiments were not conducted on the nickel blanks with much regularity, those that were conducted resulted in similar α values and indicate no serious loss in separation ability. To confirm that the observed enrichment of oxygen was due in part to the reversible binding of oxygen and not just its desorption from the complexes already formed during preparation of the membranes, the maximum amount of oxygen that could possibly be bound to the cobalt centers was calculated to be considerably less than that observed in the permeation reactions.

Facilitated transport is also demonstrated for polymer bound CoBr_2SDPT and Co_3FSDPT with slightly higher enrichment values respectively (tables 2-5 and 2-6). However, in these cases the second cycle no longer showed any enhancement, again presumably because of formation of a μ -peroxo complex or oxidation of the cobalt(II) complex. When CoSDPT was covalently attached to silica gel (0.5 millimoles/g) and added to a polystyrene membrane, a smaller degree of oxygen enrichment

was obtained (table 2-7). Second cycles of these membranes resulted in similar enrichments.

Attempts to achieve higher loadings of cobalt in the functionalized polymer were moderately successful. Data reported in tables 2-4 through 2-7 are from functionalized complexes which contain approximately 0.30% cobalt. Using more strenuous reaction conditions (elevated temperature and longer reaction time), loadings of 0.70% and 5.1% cobalt in P-CoSDPT were obtained. Permeation experiments and cycling of the membranes were carried out as reported. Comparison data are reported in table 2-8. The results indicate that with a moderate increase in loading (0.70%), an initial increase in enrichment is obtained; however, subsequent cycles are somewhat less, indicating deactivation of the metal complex due primarily to increased loading. It is not unexpected then that a loading of 5.1% had a small amount of enrichment since approximately one out of every two ligand sites was occupied. Expectedly, this should lead to a greater chance of metal-metal interaction and increased formation of μ -peroxodimers.

The incorporation of phenol (4% by weight) into the 5.1% cobalt loaded membrane resulted in lowering the oxygen enrichment for the film ($P_{O_2}^B 15 = -1.7$, $P_{O_2}^B 20 = -2.3$, and $P_{O_2}^B 25 = -2.7$ torr). It was thought that the addition of a hydrogen bonding complex such as phenol might stabilize the complex from deactivation. However, it appears that it prevents reversible oxygen binding and distorts the membrane's morphology.

The use of a more rubbery polymer, poly(butyl methacrylate), in place of polystyrene did not result in increased facilitated transport

Table 2-8. Comparison of the difference in oxygen partial pressures obtained with increased cobalt loading in PS/[P]-CoSDPT.

<u>Cobalt Loading</u>	<u>Cycle</u>	Difference in P_{O_2} (torr)		
		$P_{O_2}^B$	$P_{O_2}^B$	$P_{O_2}^B$
		<u>15</u>	<u>20</u>	<u>25</u>
0.30%	1	2.3	3.3	3.8
	2	3.5	4.3	5.0
	3	2.6	3.2	3.6
	4	-2.4	-3.5	-3.9
0.70%	1	3.6	4.5	5.7
	2	2.0	2.0	2.8
	3	2.0	2.2	2.3
5.1%	1	0.8	1.4	N.A.
	2	2.4	2.5	2.9

enrichment. Instead, it was observed that the experimental oxygen partial pressure was essentially the same or slightly lower, (oxygen enrichment at $P_{O_2}^B 15 = -1.0$, $P_{O_2}^B 20 = -0.5$, and $P_{O_2}^B 25 = -0.25$ torr), than the back-calculated non-facilitated partial pressure. This is explained by the fact that a blank poly(butyl methacrylate) membrane without any additives has a high permselectivity ($\alpha = 2.2$). Any enrichment obtained with the addition of [P]-CoSDPT is overshadowed by the increased permeability of oxygen. It is possible that this may result in fully oxygenating the cobalt complexes at very low oxygen pressures. This effectively blocks a facilitated transport mechanism. In this case the complexes act as fillers and alter the permeability of the membrane accordingly. Essentially, the rubbery polymer's diffusion mechanism dominates that of the facilitated transport.

The mechanism of oxygen transport involved in the PS/[P]-CoSDPT membranes described above is unlike that in liquid membranes. For oxygen permeation using supported metal complexes in solid polymer membranes, at least five individual processes are involved. These are shown in figure 2-9. They include within the non-facilitated process: solubility of the gas, diffusion of the gas, and desorption of it from the polymer. The facilitated path also involves oxygen binding to the metal complex, oxygen transfer to cobalt sites through the polymer, and deoxygenation of the metal complex. On the high pressure side, the attainment of equilibrium for oxygen solubility at the polymer interface is an exothermic process, as is oxygen binding to the metal center. These are not viewed as rate determining in the transport process. The importance of the metal center in the diffusion process is much more

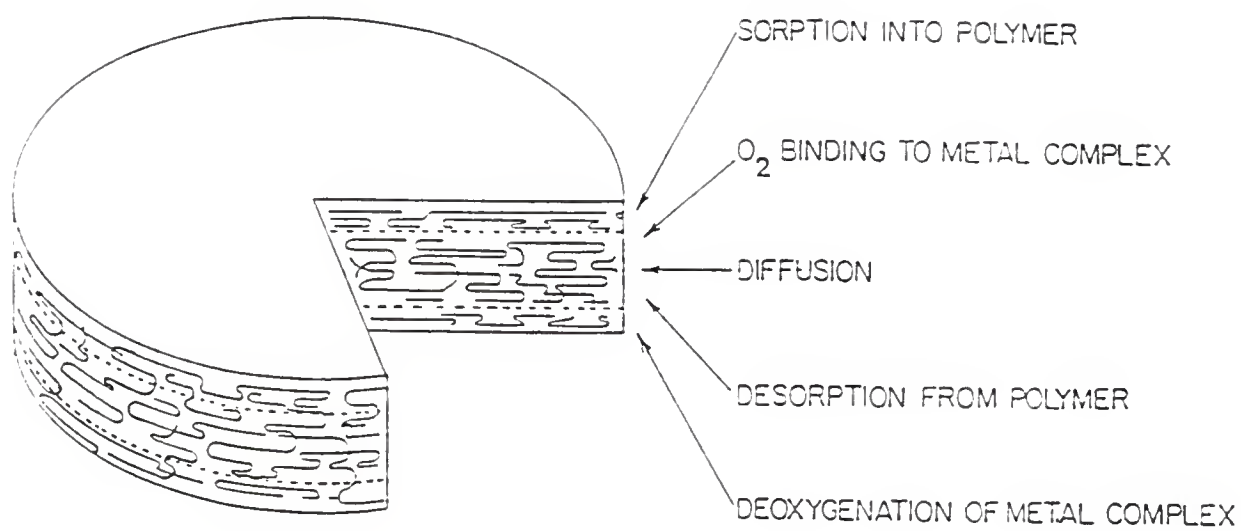


Figure 2-9. Contributions to permeation mechanism.

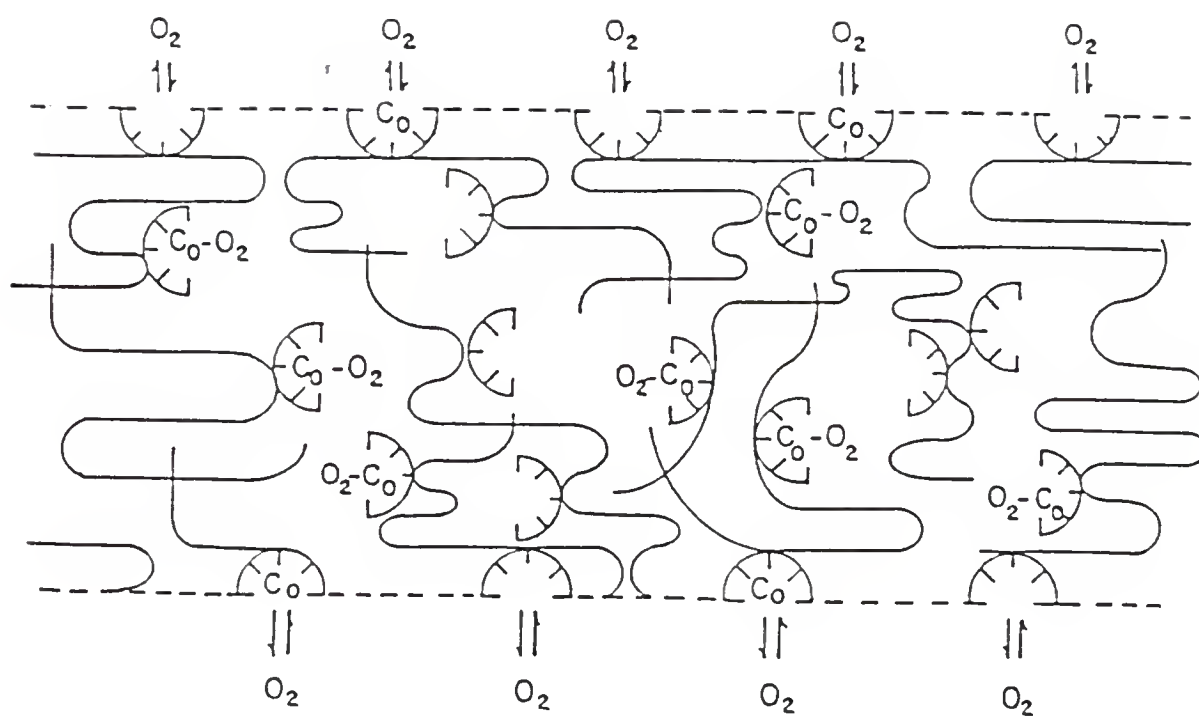


Figure 2-10. Schematic representation of a metal facilitated transport mechanism due to site to site interaction.

complex. It is proposed that the cobalt complexes transport oxygen via a site to site transfer (figure 2-10). The oxygen bound to cobalt is in equilibrium with oxygen that is soluble in the polymer maintaining a reservoir of free oxygen through the film. Cobalt-oxygen complexes on the low pressure side dissociate oxygen into the gas phase and replace it by binding oxygen from a neighboring reservoir. This necessitates a dispersion of the oxygen carriers throughout the membrane as opposed to having them only on the lower surface. The latter configuration showed no oxygen enrichment (table 2-7--Lower Surface Studies).

In conclusion, a procedure was developed for ascertaining facilitated transfer of oxygen that uses the permeation of nitrogen in the sample membrane as an internal standard. Using this, it has been demonstrated that supported cobalt complexes incorporated into a polystyrene membrane enhance the permeation of oxygen. Having accomplished these objectives, extension of the process using higher cobalt(II) loadings and rubbery polymers has failed to produce a more attractive system.

The mechanism of facilitated transport in this system differs from that in liquid membranes where diffusion of the entire complex carries oxygen across the membrane. A site to site transfer is proposed here and this mechanism requires that some of the cobalt be deoxygenated in the membrane. The $P_{1/2}$ value for CoSDPT in solution is reported⁶¹ to be 6.715×10^3 mmHg at 295 °K. A more stable adduct forms in the polymer,⁶² and its $P_{1/2}$ value determines the partial pressure of oxygen that can be attained on the lower pressure side before metal facilitated enhancement ceases.

CHAPTER III DEMONSTRATION OF THE FEASIBILITY AND VERSATILITY OF MEMBRANE REACTORS

Introduction

The previous chapter discussed some of the recent technological and commercial developments which have occurred in membrane separation processes over the past decade. The achieved results have subsequently spawned a new area of membrane development and application. Membranes are no longer being used only for separations. Increasingly, they are being extended to biochemical process applications, petrochemical operations, and inorganic membrane reactors.^{1,2}

Similarly, the work presented in this chapter has been sparked by the demonstration of transition metal complexes supported in liquid and polymer membranes for gas separations^{42-44,46-51}. The concept of permselective transport of gases by such systems has led to the use of similar membranes, or films, to catalyze reactions of gaseous substrates. A process such as this might lead to a facile separation of products from the catalyst. Additionally the selective removal of the products can shift an equilibrium system.

Even though much research is being conducted within this rapidly expanding area, the application of polymeric membrane reactors to pre-existing commercial homogeneous processes has been widely neglected. The objective of this research was twofold. The first was to

demonstrate the feasibility of a polymeric membrane reactor using well characterized catalytic reactions. The second was to apply the knowledge gained in obtaining the first goal to more reactions which utilize the advantages of a membrane reactor. The hydroformylation of propylene and the oxidation of 1-butene using transition metal compounds supported in polystyrene, poly(butyl methacrylate), and composite polystyrene/silicone gum rubber membranes were studied for demonstration purposes. The oxidation of mustard agent simulants and the formation of hydrogen peroxide were studied for application purposes.

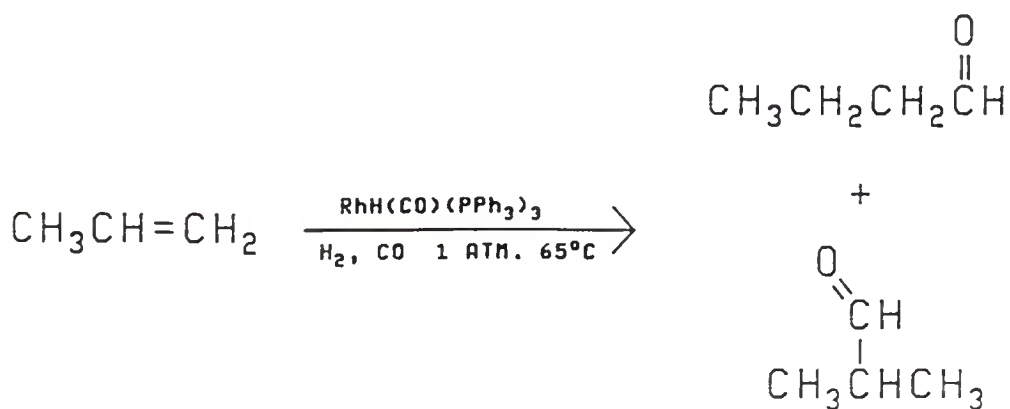
The use of insoluble, polymer bound transition metal complexes to catalyze homogeneous reactions has been reported.⁹⁻¹² A polymeric membrane reactor, however, utilizes a polymer medium for the reaction environment. This novel method of reaction has not been explored and thus investigation of its feasibility, illustration of its versatility, and elucidation of the factors which influence reactivity are warranted.

The concept of using membranes for reaction stems from attempts to combine multiple processing steps and thus achieve economically more attractive systems. The ability to conduct a reaction within a membrane along with the membrane's inherent ability for separation might eliminate several purification steps which might otherwise be necessary. To achieve this goal, layering or combining different membrane types may provide systems which allow chemical reaction and product-reactant separation within the same process unit. Hollow fiber membranes may offer another attractive pathway for improving these processes. These membranes consist of bundles of hollow fibers (10-1000 μm in diameter)

and provide extremely high surface area per unit volume, (e.g. 500 m² in a 0.3 m³ reactor).

An important aspect to be considered when investigating the feasibility of membrane reactors is how a reaction at the transition metal center is affected by the surrounding polymer environment. As in any discipline, the most useful information is obtained by comparing experimental systems and results with well characterized processes. In this case, using analogous solution chemistry as a basis for comparison gives an accurate determination of the properties associated with reaction in a membrane. Therefore, a brief description of the reactions employed will be presented. A more thorough description of hydroformylation follows in chapter 4.

Hydroformylation is the term applied to the process whereby an alkene reacts with carbon monoxide and hydrogen to form an aldehyde. This is shown schematically below. The reaction does not proceed in the absence of catalysts. Typically the catalysts or catalytic precursors employed are metal carbonyls, with cobalt and rhodium being the most widely used. The formation of butanal from propylene is the primary reaction of industrial significance.⁶³



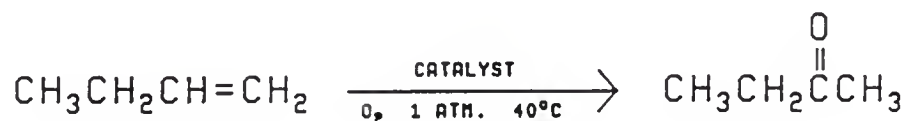
Commercially, the straight chain isomer, n-butanal, is more desirable than the branch chain isomer, isobutanal. This is mainly because of the greater number of uses and applications for n-butanal.⁶⁴ The hydroformylation reaction, or oxo process as it is known industrially, is carried out under a variety of conditions. Typical requirements when using a cobalt catalyst are total pressures of 200 to 300 atmospheres and temperatures of 120 to 170°C.⁶⁵ Use of a rhodium catalyst results in much less severe reaction conditions. Rhodium catalysts are active at room temperature and pressure.⁶⁵ Equally as important is the selectivity of products produced. Cobalt carbonyl catalysts will produce a straight to branch ratio up to three to one, while modified rhodium carbonyl catalysts can produce selectivities as high as thirty to one.⁶⁵ The relatively high activity achieved under mild reaction conditions makes rhodium an ideal catalyst for membrane reactor demonstration.

Hydridocarbonyltristriphenylphosphine rhodium(I), $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, was the complex chosen to catalyze the reaction in a polymer membrane. First reported in 1968 by Wilkinson and co-workers,⁶⁶⁻⁷¹ this homogeneous solution catalyst was shown to be active at 25°C and less than 1 atmosphere pressure. It is a precursor to the proposed active catalytic species, $\text{RhH}(\text{CO})(\text{PPh}_3)_2$, and has been shown to be one of the more active precursors. It is an ideal catalyst for demonstration purposes.

The second system chosen to demonstrate the reactor membrane process was that of an oxidation reaction. The word oxidation can be used to describe many things. Equally as diverse as the applications

and definitions are the products and mechanisms by which oxidation reactions occur. The aspect of this work is limited to a small portion of the area of oxidations and therefore the scope of material presented will be focused only upon pertinent information. There are, however, many reviews and references⁷²⁻⁷⁵ on this broad subject which are available.

Specifically, the oxidation of terminal alkenes to their respective methyl ketones, as shown below, was studied. This reaction was ideal since it offered a different type of reaction scheme from that of hydroformylation, yet was possible to achieve under mild conditions - a necessity for laboratory purposes. It also is a process which has been widely studied and well characterized and thus affords an excellent example for demonstration purposes.



The oxidation work presented in this chapter is based upon two different catalyst systems which have received considerable attention over the past twenty years. One of the first examples of selective, non-radical alkene oxidations using molecular oxygen was demonstrated by Dudley and Read in 1972.⁷⁶ It involved a stoichiometric oxidation of a terminal alkene in the presence of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ or $\text{RhCl}(\text{PPh}_3)_3$ and produced a moderately high selectivity for ketone formation relative to aldehyde. Subsequent work indicated that an equivalent quantity of

triphenylphosphine oxide was produced.⁷⁷ The system was made catalytic with the incorporation of excess triphenylphosphine ligand.⁷⁸ The selectivity of the system indicates that the reaction does not proceed by a free radical pathway. The mechanism proposed for this process is shown in figure 3-1. It essentially involves coordination of olefin, formation of a peroxo species, nucleophilic attack of the peroxo ligand on the coordinated olefin to produce a five-membered peroxymetallocycle followed by reductive elimination of the peroxymetallocycle intermediate and its subsequent decomposition to the observed products.

Another catalytic system which was found to produce selectivities in excess of 98% for methyl ketone formation was reported by Mimoun and co-workers in 1978.⁷⁹ It involves the use of a 2:1 ratio of copper(II)/rhodium(III) co-catalyst. The system is unique. Not only does it produce a high selectivity to methyl ketone, but also it involves the incorporation of both atoms of dioxygen in ketone product while exhibiting a zero order dependence for dioxygen. At 40°C, greater than 100 turnovers in four hours were achieved. It was demonstrated that the incorporation of a small quantity of isopropyl alcohol increases the activity of the reaction and results in an initial formation of acetone as a byproduct. Typically the catalyst precursors used were $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$. However many others were also employed.

Subsequent work on this system by Drago and co-workers⁸⁰⁻⁸² has shown that in the absence of a copper(II) co-catalyst, only one oxygen atom is incorporated into the ketone and that acetone and water are continuously produced. It was also demonstrated, that in the absence of

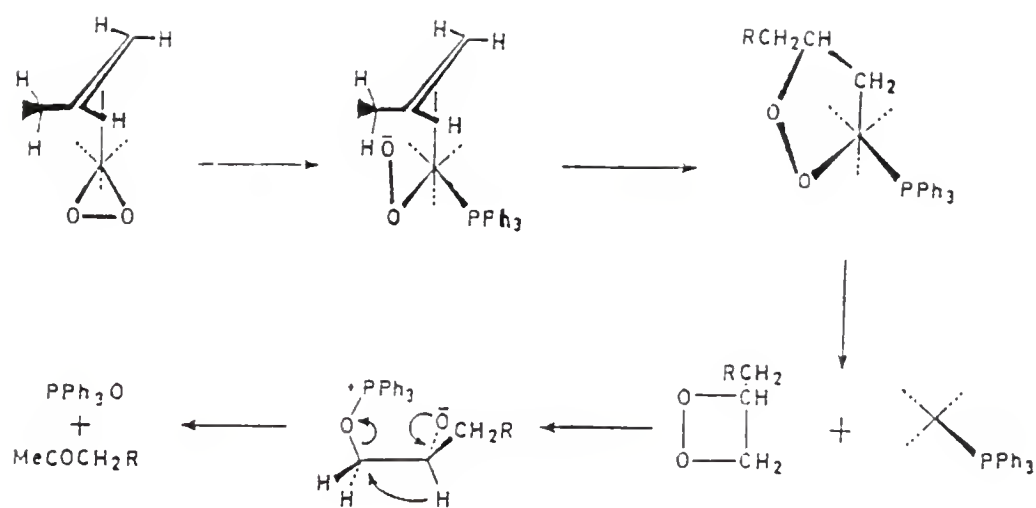
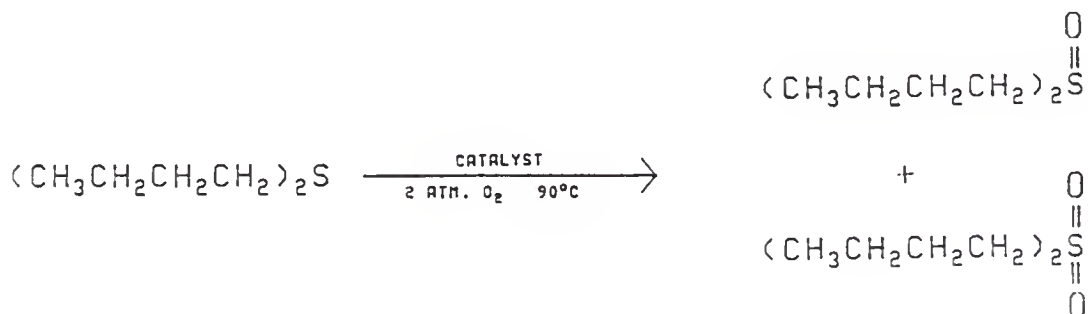


Figure 3-1. Read and Dudley mechanism⁷⁸ for the oxidation of terminal alkenes with $\text{RhH}(\text{CO})(\text{PPh}_3)_3$.

oxygen, either hydrogen peroxide or tertiary butyl hydroperoxide could be used as the oxidant. This was shown in both the systems with and without copper(II) co-catalyst. Proposed mechanisms⁸² based upon these observations are shown in figures 3-2 and 3-3.

The previously discussed reactions were utilized for demonstration purposes. Based upon the strategies and successes achieved, more advantageous systems were studied. Because of the high cost of producing and using membranes, an advantage must be gained over existing traditional technology in order to employ membranes in these reaction processes. Two reactions which might provide these advantages were tested. The first of these, the oxidation of alkyl sulfides to sulfoxides and sulfones with oxygen is shown below. The development of reactor membranes for this purpose is of particular importance. Their use as self decontamination systems is being actively investigated by the United States Army Chemical Research Development and Engineering Center. Alkyl sulfides are simulants for mustard gas agents and new routes to their decomposition are being investigated. Reactor membranes which can oxidatively decompose alkyl sulfides are being studied for their use as a polymer "self-decontaminating film" on tanks and other weaponry.



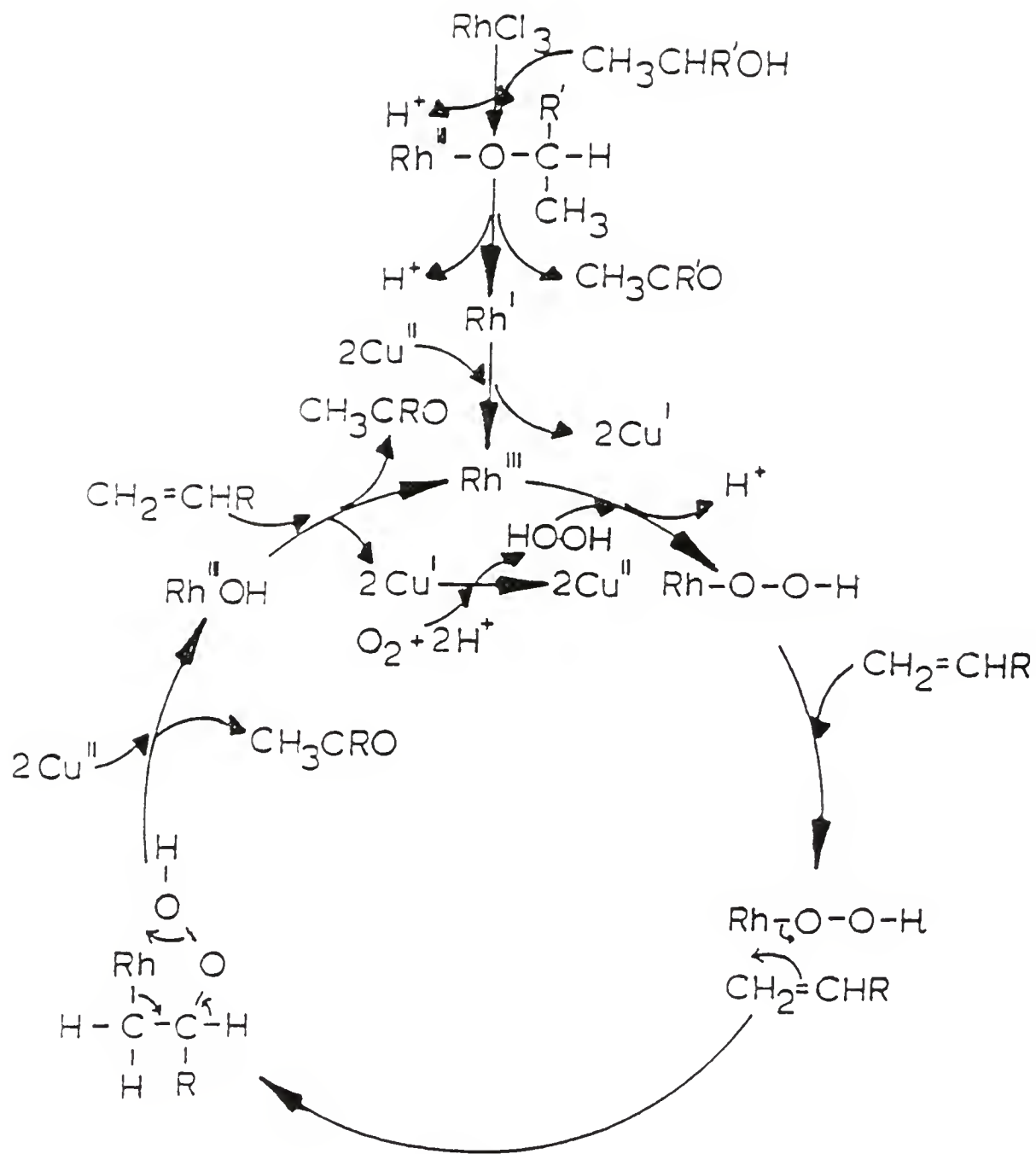
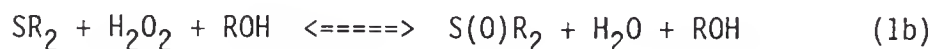
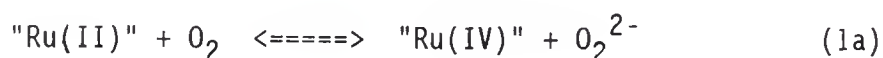


Figure 3-2.

Proposed mechanism⁸² for the oxidation of terminal alkenes using a rhodium(III)/copper(II) co-catalyst.

The selective oxidation of sulfides to sulfoxides using transition metal catalysts has been the object of an extensive quantity of research.⁸³⁻⁸⁶ Most of this reported work utilizes alkyl hydroperoxides⁸⁷⁻⁸⁹ or hydrogen peroxide⁹⁰⁻⁹³ as the oxidant and results in the formation of sulfones as a byproduct. The use of O₂ or air with these transition metal catalysts, in most cases, results in similar product formation.⁹⁴⁻⁹⁶ Ledlie and co-workers used RuCl₃•xH₂O to catalyze the oxidation of butyl sulfide.⁹⁷ Later, Riley utilized ruthenium(II) dimethyl sulfoxide catalysts in similar systems and proposed two possible mechanisms whereby a ruthenium(II)/ruthenium(IV) cycle operated.⁹⁸⁻¹⁰⁰ These are shown in the equations 1a and b, and 2.



The demonstration of ruthenium-oxo complexes in the catalysis of a variety of organic substrate oxidations¹⁰¹⁻¹⁰⁴ indicated that such catalysts might be suitable sulfide oxidation catalysts. Subsequently, Drago and co-workers have shown both cis-dioxo bis(2,9-dimethyl-1,10-phenanthroline)-ruthenium(VI)hexafluorophosphate, [Ru(O)₂(dmp)₂](PF₆)₂, and the trimer trisquo-oxo-hexapropionato-trisruthenium(III) propionate, [Ru₃O(prop)₆(H₂O)₃](prop), to be capable of oxidizing butyl sulfide to butyl sulfoxide¹⁰⁵⁻¹⁰⁷ in acetonitrile under relatively mild

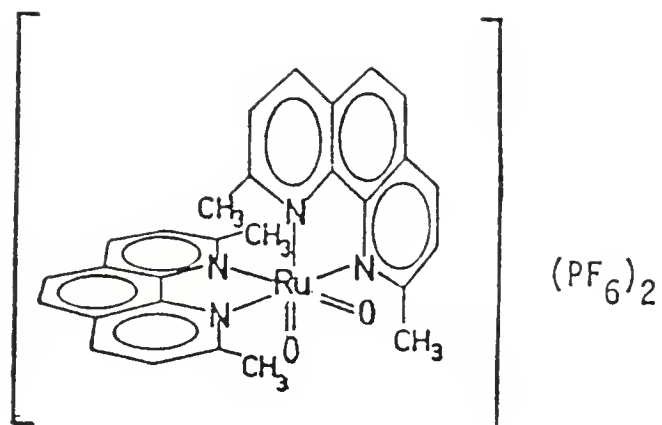
reaction conditions of 100°C and 2 atmospheres of oxygen. The catalysts are shown in figure 3-4a and b respectively.

The second application of membrane reactors is focused on the formation of hydrogen peroxide. The commercial production of hydrogen peroxide is accomplished by the anthraquinone autoxidation process¹⁰⁸ or by direct combination of hydrogen and oxygen.¹⁰⁹ Presently, there is a rapidly expanding market for hydrogen peroxide. It was estimated that 365 million pounds of H₂O₂ were used in 1987 for many different applications. The largest of these included chemical production, pulp and paper processes, and environmental purposes. It is estimated that in 1992 590 million pounds will be utilized per year.¹¹⁰ In order to keep up with such a rapidly expanding need, many companies are being forced to expand and modernize their existing plants or to develop new methods for H₂O₂ production.^{109,110}

The anthraquinone autoxidation process was first commercially operated in Germany during World War II. While many new processes have been developed, all retain the basic features of the Riedl-Pfleiderer process¹⁰⁸ shown in figure 3-5. The process involves catalytically reducing an anthraquinone to its corresponding anthraquinol which is then oxidized in air to reform the anthraquinone and produce hydrogen peroxide. The process has remained essentially the same for almost fifty years. Little improvement has been achieved in the numerous separation and purification steps which are required to maintain an active system.

The hydrogenation portion of the reaction requires a chemically stable, water insoluble, nontoxic solvent with a high flash point

a)



b)

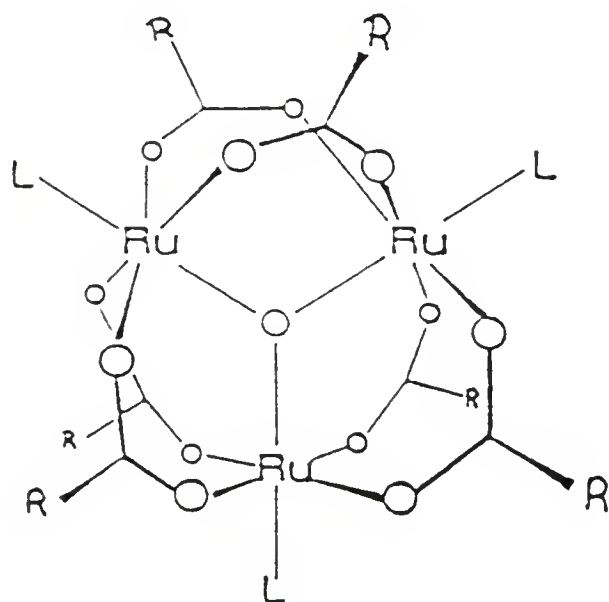


Figure 3-4. Sulfide oxidation catalysts: a) $[\text{Ru}(\text{O})_2(\text{dmp})_2](\text{PF}_6)_2$ and b) $[\text{Ru}_3\text{O}(\text{prop})_6(\text{H}_2\text{O})_3]^{3+}$.

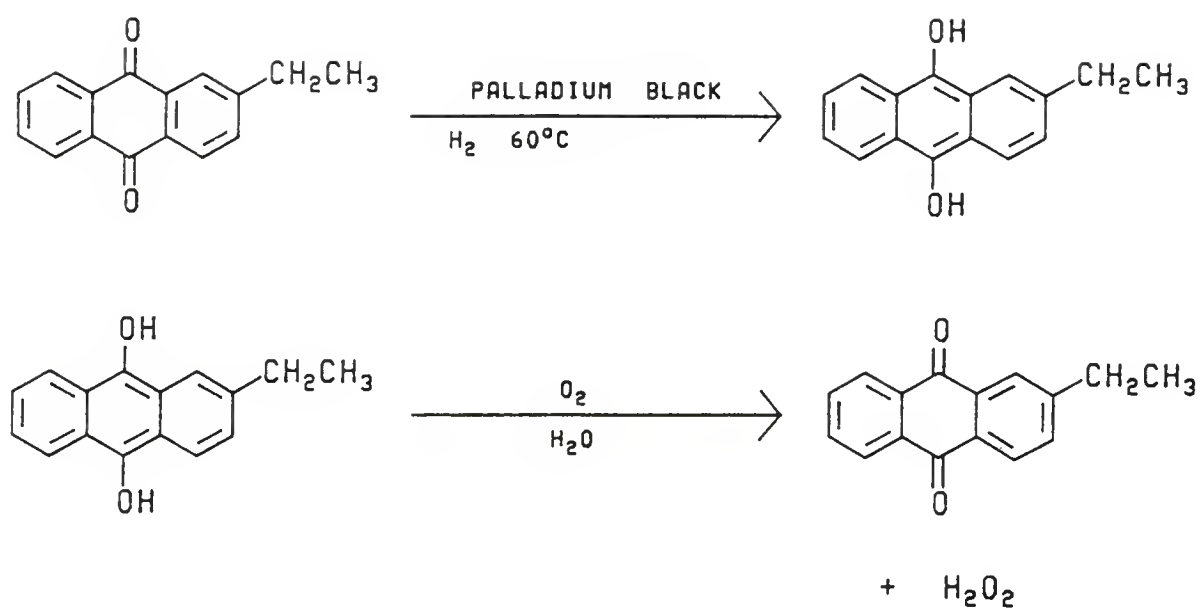


Figure 3-5. Anthraquinone autoxidation process.

and low volatility. Typically, a 50:50 mixture of benzene and $C_7 - C_9$ secondary alcohols is used. One of the major problems associated with this system involves maintaining a soluble working material. Reduction is carried out using slightly elevated partial pressures of hydrogen at temperatures under 100°C and conversion is limited to 50% to minimize anthraquinone-deactivating secondary reactions. Catalysts which have been utilized for this process step include supported Raney nickel and palladium.¹⁰⁸

The oxidation of the resulting anthrahydroquinol is easily accomplished without the aid of a catalyst. The rate is dependent upon the pressure of oxygen and temperature of the reaction. The most critical portion of this step is in the removal of the reducing catalyst and the subsequent phase boundary surface area between the organic solvent and water used for H_2O_2 extraction. Regeneration of the working solution is required to remove all inactive anthraquinone derivatives formed as well as any aqueous solution retained in the system.

A second method used for hydrogen peroxide production could be considered to be in its infancy by comparison with the anthraquinone process. Only within the past ten years has the ability to directly combine hydrogen and oxygen to produce hydrogen peroxide become available.¹⁰⁹ While little has been reported of its mechanistic detail, the procedure involved is rather straightforward. The reaction is run in an aqueous medium using palladium on adsorbent carbon as a hydrogenation catalyst with superatmospheric pressures (200 to 4000 psig) of hydrogen and oxygen. The reaction is conducted under mild temperatures (0 to 50°C) and produces an aqueous solution which is

approximately 20% H_2O_2 by weight. The use of an all-aqueous reaction medium provides a safer reaction process since it does not produce mixtures of H_2O_2 and an organic component. Application of these processes to membrane reactors may similarly produce a system which reduces the number of process steps required to maintain an active system while operating under safer reaction conditions.

The primary goal of this project was to demonstrate the ability to achieve reaction within a polymer environment and, based upon the achieved success, apply the process to reaction systems which would be advantageous for one reason or another to carry out within a membrane. The work presented supports this objective. The process developed is an extension of pre-existing catalyst technology and is not an attempt at discovering new catalysts.

Experimental

The complexes studied and/or used in this work were prepared from reagents which were either purchased or previously synthesized. The following procedures can be used to prepare these compounds. The solvents used were purified by storage over 4A molecular sieves under an atmosphere of nitrogen. Characterization of the complexes was conducted using a Nicolet 5DXB FTIR Spectrometer. Identification and quantification of reaction samples were conducted using a Varian Model 3700 gas chromatograph, a Hewlett-Packard 5890A gas chromatograph in connection with a Nicolet 5DXB FTIR Spectrometer and a Varian Model 3400 gas chromatograph in connection with a Finnigan Mat Model 700 Ion Trap

Detector. Elemental analyses were conducted by the University of Florida Department of Chemistry Microanalysis Service.

Hydridocarbonyltris(triphenylphosphine)rhodium(I), $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ –

Hydridocarbonyltris(triphenylphosphine)rhodium(I), $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, was prepared according to the literature.¹¹¹ Experimental analysis: %C = 71.8, %H = 5.12, %N = 0.00. Theoretical analysis: %C = 71.9, %H = 5.05, %N = 0.00. Melting point 120 - 122°C (lit. 121-122°C). Ir analysis (nujol mull): Rh-H: 2041 and 785 cm^{-1} (lit. 2040 and 786 cm^{-1}), C=O: 1918 cm^{-1} (lit. 1923 cm^{-1}).

Trifluoroacetatotris(triphenylphosphine)rhodium(I), $\text{Rh}(\text{O}_2\text{CCF}_3)(\text{PPh}_3)_3$

Trifluoroacetatotris(triphenylphosphine)rhodium(I), $\text{Rh}(\text{O}_2\text{CCF}_3)(\text{PPh}_3)_3$, was obtained from Dr. Cindy Getty and Steve Showalter. It can be prepared^{112,113} from $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ according to a method similar to that reported by Drago and Telser.¹¹⁴

Dioxo-bis(2,9-dimethyl-1,10-phenanthroline)ruthenium(VI) hexafluorophosphate, $[\text{Ru}(\text{O})_2(\text{dmp})_2](\text{PF}_6)_2$

$[\text{Ru}(\text{O})_2(\text{dmp})_2](\text{PF}_6)_2$ was obtained from Dr. Cindy Bailey. It can be prepared with moderate difficulty from the oxidation of $[\text{Ru}(\text{dmp})_2(\text{H}_2\text{O})_2]^{2+}$ with ceric ammonium nitrate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.^{101,115}

Trisquoahexapropionatotriscruthenium(III) propionate,

$[\text{Ru}_3\text{O}(\text{prop})_6(\text{H}_2\text{O})_3](\text{prop})$

The ruthenium trimer $[\text{Ru}_3\text{O}(\text{prop})_6(\text{H}_2\text{O})_3](\text{prop})$ was obtained from Dr. Shannon Davis. It can be prepared from $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$.¹¹⁶

Membrane Preparation

The membranes employed in this study were prepared using a casting technique. The appropriate polymer was dissolved in a suitable solvent,

most often toluene or methylene chloride. The transition metal complex to be used for a specific reaction was then dissolved in the same solvent and added to the viscous polymer solution. The resulting solution was then transferred to an aluminum foil form. Evaporation of the solvent at room temperature resulted in the formation of uniform polymer membranes with an average thickness between 0.5 and 1.0 mm. These were used without further treatment.

Permeation Apparatus

The apparatus used for the membrane reactions, (shown in figure 3-6), was designed to provide support of the membrane under experimental reaction conditions. The film is supported both on the low and high pressure sides by stainless steel metal frits (5μ pore size). Temperature of the reaction is controlled by a Variac and thermal tape in conjunction with a temperature controller.

Permeation Procedure

A typical permeation experiment is described in the following paragraph. The membrane to be used is secured between the two chambers of the reactor using o-rings and the two parts screwed together to ensure a proper seal. Both chambers are evacuated for approximately 1 hour to remove any excess solvent trapped in the membrane. The lower and upper chambers are then closed off under vacuum and the upper chamber filled with one atmosphere of the reactants. The gases permeate through the membrane during which time reaction occurs. The products and unreacted substrates then desorb from the film into the evacuated chamber. Periodically, both chambers are monitored to determine the extent of reaction. This is done using FID gas chromatography using a

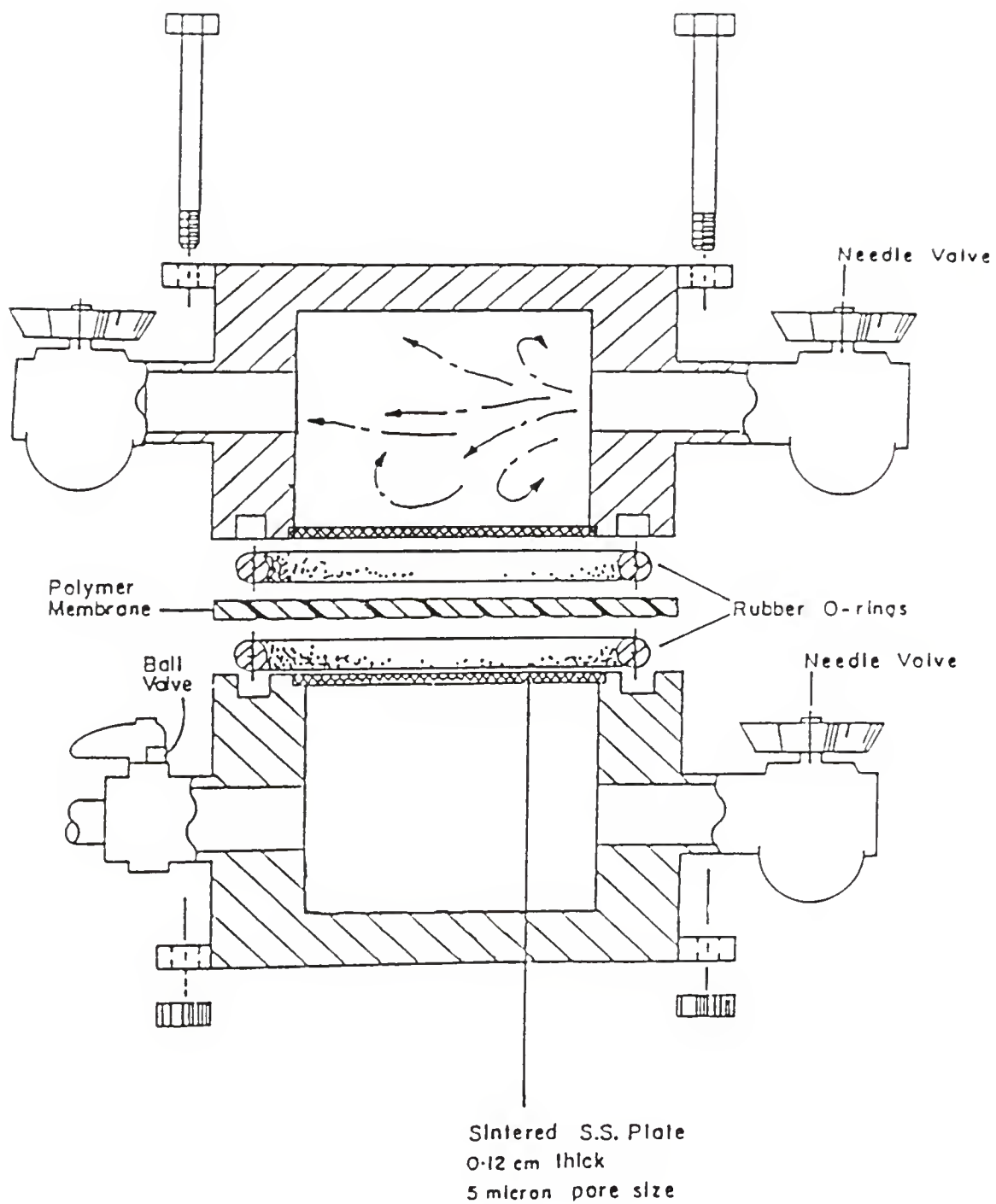


Figure 3-6. Reactor membrane apparatus.

2.5m stainless steel column packed with either porapak Q or diethyleneglycol adipate. GC-FTIR, and GC-MS were also run to confirm all of the product identities.

Results and Discussion

Hydroformylation of propylene

The hydroformylation of propylene was the first reaction attempted in order to demonstrate the reactor membrane process. The reaction was carried out at 65°C using a 1:1:1 gas mixture of the reactants hydrogen, carbon monoxide, and propylene at a total pressure of 1 atmosphere with a polystyrene membrane which contained 2.14×10^{-4} moles of $\text{RhH(CO)(PPh}_3)_3$. The pressures in the two chambers equilibrated over a period of three days. Gas samples were taken periodically, however with a decreasing pressure gradient, it is impossible to report the data on an activity curve as would normally be done with a catalytic run. Alternatively, the amount of product produced within a given period of time is reported. In this case, 4.7×10^{-10} moles of butanal and 6.6×10^{-10} moles of isobutanal was produced in 72 hours. While it is true that this is an extremely small quantity of product and represents a very small amount of conversion, it is, never-the-less important since it is the first demonstration of reaction within a polymer environment.

There are many factorss which might account for the low conversion. First, it must be considered that the reactants are gases and therefore their concentrations in the membrane are appreciably less than those of an analogous solution. The interaction of substrate and

catalyst is reduced because of this lower concentration of reactants. It is entirely possible that within the polymer, there is little catalyst substrate interaction occurring as a result of the reactants permeating through the film relatively rapidly. This is heightened by the slow diffusion of reactants within the film and the immobility of the catalyst. It is likely that a large fraction of the reactants pass through the film via pores and channels without ever coming into contact with the catalyst. Coupled with this problem is the fact that three different reactants must make contact with the catalyst for reaction to occur.

Considering this, a possible way to improve upon the extent of reaction would be to alter the diffusion and solubility characteristics of the gases in the polymer. To accomplish this, a different polymer was chosen for the reaction medium. Poly(butyl methacrylate), PBM, was the polymer chosen to demonstrate how the diffusion and solubility characteristics of the polymer could influence the reaction characteristics. Pure PBM has a glass transition temperature (T_g) of 27°C whereas the corresponding value for polystyrene is 100°C . PBM is a rubbery polymer under reaction conditions and its diffusion and solubility properties are considerably different than of polystyrene, PS, a glassy polymer under the same reaction conditions.

Using reaction conditions identical with the previously mentioned reaction, in conjunction with 3.9×10^{-5} moles of catalyst contained in the PBM film, 1.1×10^{-8} moles of butanal was produced with only trace quantities of isobutanal present. This is a remarkable observation since it demonstrates just how great an effect the polymer medium can

have on the reaction. This result can be likened to running a solution reaction in which two entirely different solvents are utilized. Perhaps the most important observation is not in the increased activity, but rather in the drastic improvement in selectivity that is achieved.

The use of a different polymer shows that the extent of reaction can be altered by changing the diffusion and solubility properties of the polymer. It was thought that a greater extent of reaction might be obtained through optimization of the reaction conditions. This can be accomplished through two means. The first involves the addition of excess ligand. The second pertains to increasing the reaction temperature and pressure. This is carried out using 2.4×10^{-6} moles of $\text{RhH(CO)(PPh}_3)_3$ in conjunction with five times as much triphenylphosphine in a PBM film at 100°C . A pressure of two atmospheres of synthesis gas (H_2 and CO), in a 1:1 ratio, is placed on both sides of the membrane and left for a period of two days. At the start of the reaction, 2.0 mL of propylene was injected into the upper chamber creating a small pressure differential (50 mmHg). This experimental setup ensures complete saturation of the membrane with synthesis gas and the partial pressure of propylene is used to facilitate its permeation through the membrane. Within twenty four hours, 2.2×10^{-7} moles of butanal are produced with trace amounts of isobutanal also observed.

The best results are achieved using a system that contains $\text{Rh(O}_2\text{CCF}_3)_3(\text{PPh}_3)_3$ in PBM with a fivefold excess of ligand under the same reaction conditions reported previously. It produces 8.1×10^{-7} moles of butanal and trace amounts of isobutanal. This catalyst had previously been studied¹¹² and shown to be efficient for the

hydroformylation of liquid substrates in solution. In this reported case, a five molar excess of triphenylphosphine in neat 1-hexene produced 225 turnovers and a 4.3 to 1 ratio of straight to branch chain aldehyde. Comparison of the polymer and solution reaction mediums reveals that they have similar dielectric constants. A summary of the membrane reactions is shown below in table 3-1.

Oxidation of 1-butene

The second system studied for demonstration purposes resulted from a serendipitous discovery. When air accidentally leaked into the initial hydroformylation system described above, the rapid production of acetone from propylene was observed. This product formation appeared to occur at a much faster rate than that of the hydroformylation products. This discovery led to attempting the oxidation of terminal alkenes to their respective methyl ketones for the demonstration of reactor membranes.

Again the first membrane studied is a PS film that contains 3.9×10^{-5} moles of $\text{RhH(CO)(PPh}_3)_3$. Reaction conditions employed were slightly milder than those of the hydroformylation systems. Temperature is maintained at 40°C and a 1 atmosphere mixture of O_2 and 1-butene is charged into the upper chamber. After three days, 7.9×10^{-9} moles of 2-butanone is produced selectively. Data for this reaction and others similar in nature are reported in table 3-2. The first thing observed with this demonstration reaction is that under milder conditions, a substantially larger quantity of product is produced relative to the similar hydroformylation system. This indicates, as expected, that different types of reactions are influenced to varying extents by the surrounding environment.

Table 3-1. Hydroformylation of propylene with $\text{RhH(CO)(PPh}_3)_3$.

<u>Membrane</u>	<u>Moles Catalyst</u>	<u>Moles Butanal</u>	<u>Turnovers^a Butanal</u>	<u>Moles Isobutanal</u>	<u>Turnovers^a Isobutanal</u>
PS ^b	2.14×10^{-4}	4.7×10^{-10}	2.2×10^{-6}	6.6×10^{-10}	3.1×10^{-6}
PBM ^b	3.9×10^{-5}	1.1×10^{-8}	2.8×10^{-4}	trace	---
PBM ^c	2.4×10^{-6}	2.2×10^{-7}	9.2×10^{-2}	trace	---
PBM ^d	2.4×10^{-6}	8.1×10^{-7}	3.4×10^{-1}	trace	---

^a turnover is moles of product/mole of catalyst.

^b reaction conditions are 65°C, 1 atm. H_2 , CO, and propylene (1:1:1 mix) in the upper chamber, and reaction time is three days.

^c membrane contains 1.2×10^{-5} moles triphenylphosphine at 100°C. Both chambers contain 1 atm. of H_2 , CO (1:1 mix). Upper chamber contains an additional 2.0 mL of propylene (1 atm. pressure). Reaction time is one day.

^d $\text{Rh(O}_2\text{CCF}_3)(\text{PPh}_3)_3$ catalyst in place of $\text{RhH(CO)(PPh}_3)_3$ under identical conditions to note c. Reaction time is one day.

Table 3-2. Oxidation of 1-butene.

<u>Membrane</u>	<u>Catalyst</u>	<u>Conditions</u> ^a	<u>Moles 2-butangne (x 10⁹)</u>	<u>Turnovers 2-butangne (x 10⁴)</u>
PS	RhH(CO)(PPh ₃) ₃		7.9	2.0
PS	RhH(CO)(PPh ₃) ₃	2nd cycle	14.	3.6
PBM	RhH(CO)(PPh ₃) ₃		12.	3.1
PBM	RhH(CO)(PPh ₃) ₃	2nd cycle	47.	12.
PBM	RhH(CO)(PPh ₃) ₃	60°C	24.	6.2
SGR/PS	Rh(III)/Cu(II) ^b		200.	25.
PBM	Rh(III)/Cu(II) ^b	60°C	160.	20.
PBM	RhH(CO)(PPh ₃) ₃	1-hexene	240.	62.

^a standard reaction conditions: 3.9×10^{-5} moles catalyst at 40°C with 1 atm. O₂ and 1-butene (1:1 mix). Reaction time is three days.

^b 8.0×10^{-5} moles RhCl₃•xH₂O and 1.6×10^{-4} moles Cu(NO₃)₂•2.5H₂O.

The same quantity of catalyst as was used in the previous reaction was supported in a PBM film. Under similar reaction conditions, an increase in the amount of product was observed. In this case, 1.4×10^{-8} moles of 2-butanone was produced. Cycling experiments were conducted by reevacuating each system and refilling the upper chambers with reactants. Essentially all membranes are saturated with reactants at the start of the second cycle. This results in almost a twofold increase in the production of 2-butanone for the polystyrene system and nearly a fourfold increase with poly(butyl methacrylate). Again this is best explained by the theory that saturation of the membranes with reactants has occurred resulting in increased catalyst-substrate interaction. Improved reactivity is the end result of this increased interaction. Raising the reaction temperature to 60°C while using the PBM/RhH(CO)(PPh₃)₃ membrane also improves reactivity in the butene system. This is expected for a temperature dependent reaction.

Another reaction using the liquid substrate 1-hexene was conducted to verify that higher substrate concentration within the membrane would indeed result in increased reactivity. Five drops of the substrate was placed on the film and the reaction run with the same quantity of catalyst and reaction conditions. In three days, 2.40×10^{-7} moles of 2-hexanone are produced selectively. This lends support to the idea that the reactivity of the membrane can be increased dramatically under more solution-like reaction conditions.

Based upon the observed results, a mechanistically different reaction was attempted. It involved the use of a Rh(III)/Cu(II) co-catalyst system in the oxidation of terminal alkenes. A silicone gum

rubber polymer containing 8.0×10^{-5} moles of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ and 1.6×10^{-4} moles of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ along with a approximately 1.0 ml of isopropanol was layered on a polystyrene blank membrane. This resulted in the production of 2.0×10^{-7} moles of 2-butanone in 72 hours. The same catalyst system contained in a PBM film at 60°C was not quite as reactive (1.60×10^{-7} moles in 72 hours). These observations show that mechanistically different reactions such as this can be very active. This supports the conclusion that the reaction type itself plays a large part in determining the extent of reaction within the polymer framework.

Oxidation of butyl sulfide

Based upon the successes achieved in the above reactions, attention next turned towards processes in which membrane use may be more economically attractive. The catalytic oxidation of the simulant butyl sulfide is studied with (1) $\text{Ru}(\text{Cl})_2(\text{PPh}_3)_3$, (2) $[\text{Ru}(\text{O})_2(\text{dmp})_2](\text{PF}_6)_2$, and (3) $[\text{Ru}_3\text{O}(\text{prop})_6(\text{H}_2\text{O})_3](\text{prop})$ in polystyrene/silicone gum rubber composite membranes. Composite catalyst membranes are obtained by evaporating a catalyst/silicone gum rubber/toluene solution onto a preformed blank polystyrene film. The ruthenium membrane oxidations of butyl sulfide are carried out by coating the upper side (the side exposed to the higher pressure) of the films with a small amount of the liquid substrate. The top chamber of the reactor is then filled with 30 psi O_2 and the bottom chamber is closed off under vacuum. Temperature of the reaction is maintained at 90°C . The pressures within the two chambers equilibrate over a period of two days. The gas which collects in the bottom chamber is determined to contain large percentages of butyl sulfoxide, butyraldehyde, and

propionaldehyde, along with a small quantity of unreacted butyl sulfide. Trace quantities of 1-butene and 1,2-epoxybutane are also observed using GC-MS.

In all membrane reactions, the total amount of products formed appears to be substantially smaller in comparison with solution data. A better method of analysis in this particular case would be to compare the percentage conversion of butyl sulfide. In analyzing these membrane reactions, the percent conversion is based upon the amount of butyl sulfide and products which have passed through the membrane and not on the original amount exposed to the film. This is the most relevant mode of analysis since the employment of these materials as self decontaminating films focuses only on the gases which permeate the film and their relative amounts.

Table 3-3 lists the mole percent conversion for each of the composite membrane catalysts systems. It should be noted that a modified reactor design employing a smaller film with less catalyst is used in the phenanthroline derivative system. In light of this, a better judge of the membrane activities is made by comparing turnovers of the respective catalyst membranes. A turnover is defined as the number of moles of product produced per mole of catalyst. This gives an accurate representation of the reaction assuming that an excess amount of substrate was exposed to each film. Turnover data is presented in table 3-4 and indicates that the ruthenium trimer is the best overall catalyst employed in the membranes. Evidence which supports the theory that a large quantity of substrate may never come in contact with the

Table 3-3. Butyl sulfide membrane conversion data for various ruthenium catalyzed oxidations by O_2 at 1 atm. and $90^\circ C$.

<u>Reaction Time (hrs)</u>	<u>Mole Percent</u>				<u>Total Conversion</u>
	<u>Butyl Sulfide</u>	<u>Butyl Sulfoxide</u>	<u>Butanal</u>	<u>Propanal</u>	
<u>Ru(Cl)₂(PPh₃)₃</u>					
0	--	--	--	--	--
24	2.8	11.3	40.0	45.9	97.2
48	1.9	15.5	40.0	42.6	98.1
<u>[Ru₃O(prop)₆(H₂O)₃](prop)</u>					
0	--	--	--	--	--
24	10.8	1.4	2.0	85.8	89.2
42	3.6	0.2	0.3	95.9	96.4
<u>[Ru(O₂)₂(dmp)₂](PF₆)₂</u>					
0	--	--	--	--	--
24	85.6	1.2	13.2	--	14.4
48	78.0	2.6	19.4	trace	22.0

Table 3-4. Butyl sulfide membrane turnover data.

<u>Catalyst</u>	<u>Turnovers (x 10²)</u>			
	<u>Butyl Sulfoxide</u>	<u>Butanal</u>	<u>Propanal</u>	<u>Total</u>
$\text{Ru}(\text{Cl})_2(\text{PPh}_3)_3$	0.27	0.97	1.11	2.35
$[\text{Ru}_3\text{O}(\text{prop})_6(\text{H}_2\text{O})_3](\text{prop})$	1.00	1.49	63.70	66.19
$[\text{Ru}(\text{O})_2(\text{dmp})_2](\text{PF}_6)_2$	0.40	4.68	---	5.08

Turnover data are reported at a reaction time of 24 hours based on data in table 3-3.

catalyst in the membrane is obtained by comparing tables 3-3 and 3-4. It is apparent that a larger conversion percentage can be obtained by increasing the catalyst loading in the membrane and thus increasing the extent of interaction between substrate and catalyst.

Comparison of the membrane data can be made to their solution analogues¹⁰⁶ as well. Reported mole percent conversions of butyl sulfide for the three ruthenium catalysts in solution under similar reaction conditions is presented in table 3-5. The relatively high percentage of conversion compared to solution studies indicates that reactor membranes may prove to be useful as self decontamination systems. The data obtained is very encouraging and indicates that the catalyst is active when incorporated into a polymer network. Though the activity of the membranes is lower than the solution systems, based on the amount converted per unit time, the high conversion of material passing through film is a desired result.

Formation of hydrogen peroxide

The production of hydrogen peroxide has been accomplished by the anthraquinone autoxidation process and by direct combination of hydrogen and oxygen. The application of these two systems to membrane reactors is yet another process which has shown membrane reactors to be a versatile process. One part of this research incorporates the basic reaction scheme outlined in the introduction. As noted earlier, a major drawback associated with the anthraquinone autoxidation process is maintaining a soluble system. Several reaction and separation steps are needed to maintain an active process. This work represents a novel

Table 3-5. Butyl sulfide solution reaction conversion data for various ruthenium catalyzed oxidations by O_2 at $90^\circ C$.

<u>Reaction Time (hrs)</u>	<u>Butyl Sulfide</u>	<u>Mole Percent</u>			<u>Total Conversion</u>
		<u>Butyl Sulfoxide</u>	<u>Butanal</u>	<u>Propanal</u>	
<u>Ru(Cl)₂(PPh₃)₃</u>					
0	100	--	--	--	0
12	49.7	50.3	--	--	50.3
36	40.9	59.1	--	--	59.1
<u>[Ru₃O(prop)₆(H₂O)₃](prop)</u>					
0	97.4	2.6	--	--	2.6
12	77.2	22.8	--	--	22.8
37	59.7	40.7	0.6	--	41.3
<u>[Ru(O₂)₂(dmp)₂](PF₆)₂</u>					
0	99.3	--	0.7	--	0.7
12	72.1	25.9	2.0	--	27.9
36	69.1	28.1	2.8	--	30.9

Source of data is reference 106.

approach aimed at minimizing the number of required process steps while maintaining the solubility and stability of the working material in both its oxidized and reduced states. This would result in a more economically attractive system. The reaction is conducted by incorporating the catalytic system into a rubbery polymer membrane, PBM, which is used as the medium for reaction. The second system under investigation, the direct combination of oxygen and hydrogen, is performed by incorporating a palladium catalyst into a PBM membrane and using it as the reaction medium.

Flat reactor membranes are formed from poly(butyl methacrylate) using a casting technique. Depending upon the system being studied, either palladium black or a mixture containing 2-ethyl anthraquinone and palladium black are incorporated in the polymer membrane. A different apparatus than was used in the previous systems is used to support the reaction. It is shown in Figure 3-8 and consists of two glass chambers. The membrane is sealed between them using an O-ring joint and clamp. The reaction is facilitated by passing hydrogen gas over the bottom side of the membrane and by saturating an aqueous solution on the top side of the membrane with oxygen. Reaction occurs as the two gases diffuse into the membrane and come in contact with the catalyst system. The temperature of reaction is maintained by placing the reactor in an oil bath at the desired temperature. A slightly positive pressure of hydrogen is maintained in the lower chamber. Reaction occurs over a four day period. The resulting hydrogen peroxide is extracted into the aqueous layer and titrated with potassium permanganate to determine the extent of reaction.

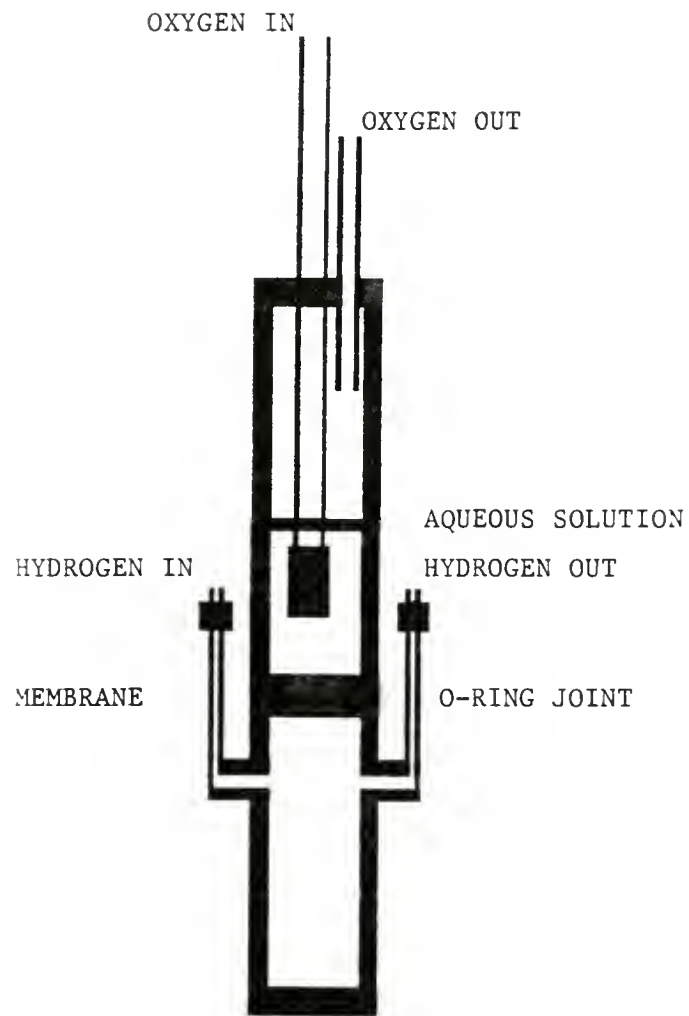


Figure 3-7. Hydrogen peroxide membrane reactor.

There are several key variables in this process that have been investigated. Included among these are temperature dependence of the process, the effect of added promoters, and the effect of cycling the membranes. Data for the performed reactions are contained in table 3-6. The results indicate that the anthraquinone systems are the most active. Increased temperature also results in a more active system. Reaction using only palladium black was accomplished with comparable activity to the anthraquinone system. The best system for direct combination of hydrogen and oxygen is one which incorporates an acid and halide promoter in the film and employs higher reaction temperatures. Attempts to find a more active system using a palladium colloid suspended in a polymer film failed when the poly(vinyl alcohol vinyl acetate) membrane used in the reaction dissolved during reaction.

In conclusion, the comparison of all membrane reactions with their respective homogeneous analogues results in some notable distinctions. The membrane reactions appear to be substantially less reactive. This is due largely in part to the relative amount of time that the substrate spends in contact with the catalyst. A possible way of improving upon this would be to increase catalyst concentration. A thicker membrane might also provide for better interaction. Comparatively, a solution reaction occurs with the substrate continuously diffusing in and out of solution. This results in an infinite amount of exposure with the catalyst. In a membrane reaction, the substrate is contained in the film for a much smaller amount of time, effectively limiting the extent of reaction. Another observation that would explain the difference in the reactivities of membrane and solution reactions is the relative

Table 3-6. Hydrogen peroxide formation.

<u>CATALYST</u>	<u>PROMOTER</u>	<u>REACTION CONDITIONS</u>	CYCLES (moles $\text{H}_2\text{O}_2 \times 10^6$)			
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Pd BLACK & 2-ETHYL ANTHRAQUINONE	NONE	60°C	2.2	2.2	1.1	1.2
Pd BLACK & 2-ETHYL ANTHRAQUINONE	NONE	95°C	11.	12.	6.9	
Pd BLACK	NONE	60°C	0.9			
PD BLACK	H^+ , Br^-	60°C	1.1			
Pd BLACK	NAFION, H^+ , Br^-	60°C	1.7	1.7	0.9	
Pd BLACK	NONE	85°C	1.6	1.4		
Pd BLACK	H^+ , Br^-	85°C	1.5	1.8	1.5	
Pd BLACK	NAFION, H^+ , Br^-	85°C	2.0	1.0	2.0	1.2

Reaction conditions: PBM film layered on PS, 20.0 mL aqueous solution for four day cycles. $[\text{H}^+] = 1 \text{ M HCl}$, $[\text{Br}^-] = 1.3 \times 10^{-3} \text{ M KBr}$, 3.6×10^{-4} moles Pd black, and/or 1.5×10^{-4} moles 2-ethyl anthraquinone.

difference in substrate concentrations contained in each reaction medium. This directly affects the number of catalyst substrate interactions which occur.

The initial objective of this project has been obtained. Demonstration of the feasibility and versatility of transition metal reactor membranes has been achieved with both hydroformylation and oxidation reactions. The activities of the membranes are low as a result of the engineering design of our experiment. The use of hollow fiber membranes may lead to a more productive system. For example, the best hydroformylation system studied produces 8.1×10^{-7} moles of butanal in 24 hours or 4.06×10^{-8} g of butanal per minute using a film with a surface area of $5.0 \times 10^{-4} \text{ m}^2$. A typical hollow fiber membrane unit using $100\mu\text{m}$ fibers contained in a 0.3 m^3 reactor has a surface area of 500 m^2 . Transposing our system to this reactor would produce 4.0×10^{-2} g of butanal per minute. This may be one way of increasing production capabilities in membrane reactors. Optimization of reaction conditions has been shown to result in remarkable increases in reactivity.

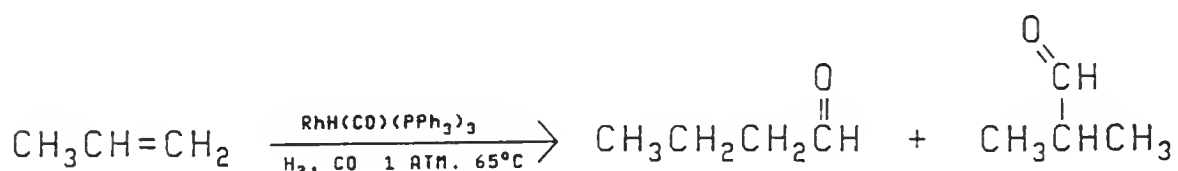
CHAPTER IV HETEROGENEOUS HYDROFORMYLATION OF PROPYLENE USING SUPPORTED RHODIUM CATALYSTS IN A CONTINUOUS GAS FLOW REACTOR

Introduction

The previous chapter demonstrates the feasibility and versatility of facilitating chemical reactions within an organic polymer environment. One remarkable attribute of membrane reactions lies in their ability to achieve high selectivity for a particular product. This is evidenced in the hydroformylation of propylene to n-butanal with a high degree of selectivity. A major drawback that is associated with these membranes is in their extremely low activity. The work presented in this chapter involves the development of a gas phase, heterogeneous catalyst based system resulting in substantially increased activity while maintaining the selectivity associated with the polymer membrane reactors.

The hydroformylation of propylene is the reaction chosen to demonstrate this objective. The ability to use a gaseous substrate, the possibility of producing either straight or branched chain product, and the availability of a catalyst which is active under moderate reaction conditions makes it ideal for study. The reaction is previously described in chapter 3. A more detailed discussion of the reaction is presented in this section.

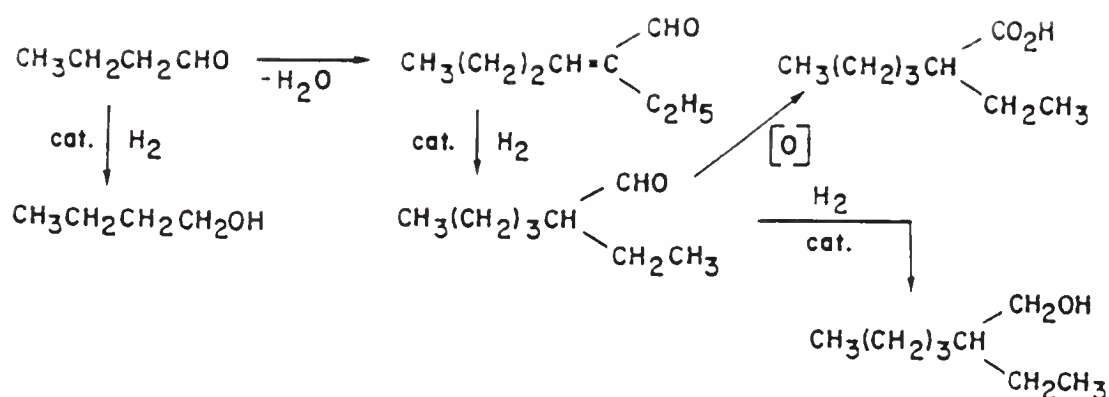
Hydroformylation is the process whereby an alkene reacts with carbon monoxide, CO, and hydrogen, H₂, to form an aldehyde. The hydroformylation of propylene results in the formation of both n-butanal and isobutanal as shown below.



The reaction does not proceed in the absence of a catalyst. Commercially, two transition metals, cobalt and rhodium, are used to form active catalyst complexes and are usually employed as the metal carbonyl complexes. First discovered by Otto Roelen in 1938,¹¹⁷ the process has since grown to immense proportion. In 1980, over eight billion pounds of aldehydes or their derivatives were produced by the process, with the formation of butanal from propylene being the primary reaction scheme.⁶³

Commercially, the straight chain isomer, n-butanal, is more desirable than the branched chain isomer, isobutanal. This is because of the greater number of uses and applications for n-butanal.⁶⁴ As shown below, n-butanal can be converted through a variety of steps to n-butanol and 2-ethylhexanol. The latter can be converted into plasticizers for polyvinylchloride resins.

The hydroformylation reaction, or oxo process as it is known industrially, can be achieved using a variety of conditions. Typical requirements for a cobalt catalyst system require total pressures of 200

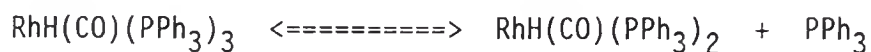


to 300 atmospheres and temperatures of 120 to 170°C.⁶⁵ Use of rhodium catalysts result in much less severe reaction conditions. Activity can be observed using room temperature and pressure.⁶⁵ Equally as important is the selectivity. Cobalt carbonyl catalysts produce a straight to branch ratio up to three to one, while modified rhodium carbonyl catalysts produce selectivities as high as thirty to one.⁶⁴ The selectivity obtained is dependent upon a number of factors including the ligand environment of the metal, the presence of excess ligand in the system, and the pressure of gaseous reactants used. The relatively high activity achieved under mild reaction conditions makes rhodium an ideal catalyst for continuous gas flow reactor demonstration.

Modified rhodium oxo catalysts were introduced into commercial use in 1976.¹¹⁸⁻¹²⁰ One of these, hydridocarbonyltristriphenylphosphine rhodium(I), $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, was the catalyst chosen to catalyze the reaction. First reported in 1968 by Wilkinson and associates,⁶⁶⁻⁷¹ this homogeneous catalyst was shown to be active at 25°C and less than 1 atmosphere pressure. It is a precursor to the proposed active catalytic

species, $\text{RhH(CO)(PPh}_3)_2$, and has been demonstrated to be one of the more active rhodium precursors. It does not react to form inactive metal clusters like many other rhodium carbonyl complexes.

Selectivity is controlled by a number of factors. The use of polar solvents as the reaction medium leads to increased reactivity and produces increased selectivity.¹²¹ Most importantly, the addition of excess triphenylphosphine results in increased linear selectivity. The reaction has even been carried out in molten triphenylphosphine.⁶⁴ A disadvantage though, is that the rate of hydroformylation decreases with the addition of excess phosphine. The increase in selectivity has been attributed to increased steric hinderance while the decreased activity can be explained by the effect of shifting the equilibrium from a proposed active catalytic species towards the precursor. This equilibrium is shown in the equation below.



The widely accepted mechanism of this reaction is depicted in figure 4-1. As shown, the reaction can occur by either a dissociative or associative pathway with the first step being the subsequent dissociation of a triphenylphosphine ligand.⁶⁵ Coordination of carbon monoxide is the next proposed step. Next, olefin coordination occurs. It is the most critical step. Subsequent addition of the olefin to the rhodium hydride bond determines whether linear or branched chain aldehyde is formed. Markonikov addition results in the formation of a branched alkyl complex, while anti-Markonikov addition results in the

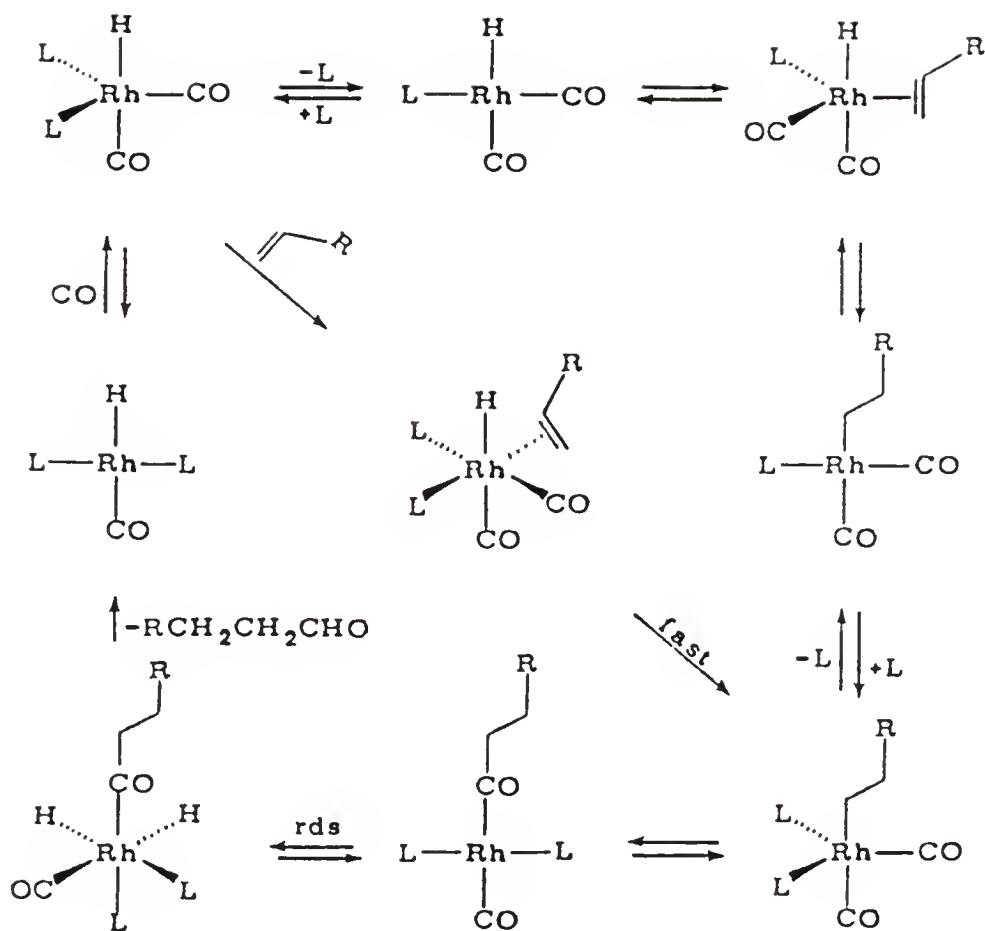


Figure 4-1. Associative and dissociative hydroformylation reaction mechanism.

formation of a linear alkyl complex. Carbon monoxide migration and insertion to form the acyl complex is the next proposed mechanistic step. This is followed by the oxidative addition of hydrogen.¹²² The latter step is thought to be rate determining in the reaction but it remains uncertain.⁶⁵ Reductive elimination of aldehyde results in reformation of the catalytic species.

Hydroformylation using modified rhodium catalysts results produces a rather complex system. Many Rhodium species have been observed in these systems including $\text{RhH(CO)(PPh}_3)_3$, $\text{RhH(CO)(PPh}_3)_2$, $\text{RhH(CO)}_2(\text{PPh}_3)_2$, and $\text{RhH(CO)}_2(\text{PPh}_3)$.¹¹⁸ These complexes exist in equilibrium with each other and are formed from either triphenylphosphine dissociation or CO addition. The truly active species has not been determined but may be any one or combination of these in solution.

The high cost of rhodium has limited its use commercially. Development of a process which alleviates catalyst recovery problems associated with conventional homogeneous systems while achieving high selectivity and activity will result in an economically more viable reaction process. A considerable effort has been devoted to modifying homogeneous based rhodium catalysts to form heterogeneous catalysts. This would offer immediate advantages in catalyst/product separations. Use of insoluble supported catalysts in liquid phase reactions or vapor phase reactions over supported catalysts might achieve this desired objective.

Attempts to form heterogeneous oxo catalysts by attaching them to supports through their phosphine ligands has not resulted in better catalytic systems.¹²³⁻¹²⁵ Use of these supported catalysts in liquid

phase reactions leads to active and selective systems, however, catalyst leaching occurs. Cleavage of the phosphorous carbon bonds used to attach the catalysts results in degradation of supported complexes providing a pathway for catalyst leaching from the support.^{126,127}

An effective gas phase system is reported by Arai and co-workers.¹²⁸ The process utilizes silica gel as a support. It is covered with a polymer formed from styrene and divinylbenzene and then functionalized with phosphine ligands. Chlorocarbonylrhodium(I) dimer, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, is then supported on its surface. This catalyst is found to be effective in hydroformylating both ethylene and propylene at 100°C with atmospheric pressures of gaseous reactants. One of the major drawbacks associated with this system is in the low selectivity obtained for the production of n-butanal (63%) from propylene. The phosphine linkage was viewed to be important since direct deposition of $(\text{PPh}_3)_2\text{Rh}(\text{CO})\text{Cl}$ and RhCl_3 on silica exhibited little activity under similar conditions. Deposition of $(\text{PPh}_3)_2\text{Rh}(\text{CO})\text{Cl}$ on alumina and activated charcoal, however, produces active systems under substantially more severe reaction conditions.¹²⁹ Again low selectivities for the linear aldehyde are obtained (56.5 to 65.5%). Gas phase hydroformylation of ethylene and propylene have also been achieved over zeolite supported rhodium catalysts.¹³⁰⁻¹³² Again the selectivity of these systems is poor (<67% linear aldehyde) and the simultaneous hydrogenation of propylene and aldehyde is a severe problem.

The objective of the work presented in this chapter is to extend what has been accomplished with membrane based reactors. This is achieved by the development of a heterogeneous catalyst based system

which produces substantially increased activity while maintaining the intrinsic benefits associated with the polymer membranes, namely their selectivity. This is accomplished by deposition of a rhodium catalyst and excess phosphine ligand on silica gel and its use in a gas phase, continuous flow reaction. The development of a reactor which is connected to a gas chromatograph ("on-line GC") results in an accurate evaluation of the reaction properties. Modification of the catalyst system by coating with a polar, nonvolatile system results in increased activity and selectivity.

Experimental

The transition metal catalysts studied in this work are prepared as previously described in chapter III. Identification and quantification of reaction samples are conducted using a Perkin Elmer model 900 gas chromatograph placed in conjunction with a continuous flow gas reactor. This is more simply described as an "On-line" gas chromatograph.

Catalyst Preparation

The catalysts employed in this study are prepared by dispersion on a solid support in the presence of an excess quantity of triphenylphosphine ligand. A typical description of this procedure is detailed below. A 250 mL round bottom flask is charged with 0.600g of silica gel (vacuum dried at 80°C), 0.0919g (1.000×10^{-4} moles) $\text{RhH(CO)(PPh}_3)_3$, and .262g (1.00×10^{-3} moles) triphenylphosphine. Twenty five milliliters of chloroform is added to the solid mixture and

the solution stirred for approximately five minutes. It is then rotary evaporated giving a yellow granular product which is vacuum dried overnight at 45°C. Catalysts which are coated with propylene carbonate are prepared similarly with the propylene carbonate being dissolved in the chloroform before its addition to the solid catalyst mixture. A brief description of the preparation of all catalyst systems investigated is listed below. Each is identified by its appropriate abbreviation throughout the remainder of the text.

RhH\SG

The catalyst is prepared by dispersion of 0.230g (2.50×10^{-4} moles) $\text{RhH(CO)(PPh}_3)_3$ and 0.656g (2.50×10^{-3} moles) triphenylphosphine, PPh_3 , on 1.50g of silica gel using the method outlined above.

RhH\SG\PC

The catalyst is prepared by dispersion of 0.0919g (1.00×10^{-4} moles) $\text{RhH(CO)(PPh}_3)_3$ and 0.262g (1.00×10^{-3} moles) triphenylphosphine and 0.08g of propylene carbonate on 0.600g of silica gel using the method described above.

RhH\MPPS

The catalyst is prepared by dispersion of 0.0919g (1.00×10^{-4} moles) $\text{RhH(CO)(PPh}_3)_3$ and 0.262g (1.00×10^{-3} moles) triphenylphosphine on 0.600g of macroporous polystyrene beads using the method outlined above.

RhH\MPPS\PC

The catalyst is prepared by dispersion of 0.0919g (1.00×10^{-4} moles) $\text{RhH(CO)(PPh}_3)_3$ and 0.262g (1.00×10^{-3} moles) triphenylphosphine

and 0.08g of propylene carbonate on 0.600g of silica gel using the method described above.

RhH\Nafion

The catalyst is prepared by dispersion of 0.0919g (1.00×10^{-4} moles) $\text{RhH(CO)(PPh}_3)_3$ and 0.262g (1.00×10^{-3} moles) triphenylphosphine on 0.600g of ground nafion using the method outlined above.

Rh(tfa)\SG

The catalyst is prepared by dispersion of 0.253g (2.50×10^{-4} moles) $\text{Rh(tfa)(PPh}_3)_3$ and 0.656g (2.50×10^{-3} moles) triphenylphosphine on 1.50g of silica gel using the method outlined above.

Rh(tfa)\SG\PC

The catalyst is prepared by coating 0.92g of the previously prepared $\text{Rh(tfa)\SG}$ with 0.08g of propylene carbonate. This is accomplished by rotary evaporation as described above in the catalyst preparation section. This provides the exact quantities of reagents used in the preparation of the other catalysts.

Reaction Procedure

The reaction is conducted in a stainless steel tube connected in line with a GC as noted above. A schematic diagram of this setup is shown in figure 4-2. The tube is 1/8" chromatography tubing, 45cm in length with approximately a 25cm catalyst bed height. It is packed with 0.500g of the catalyst. A preblended lecture bottle of H_2 , CO, and propylene is used to deliver the gases to the reactor. The flow and internal pressure of the gases are controlled by valves positioned before and after the reactor tube. Reaction temperature is controlled by an oil bath. The extent of reaction is determined using a sample

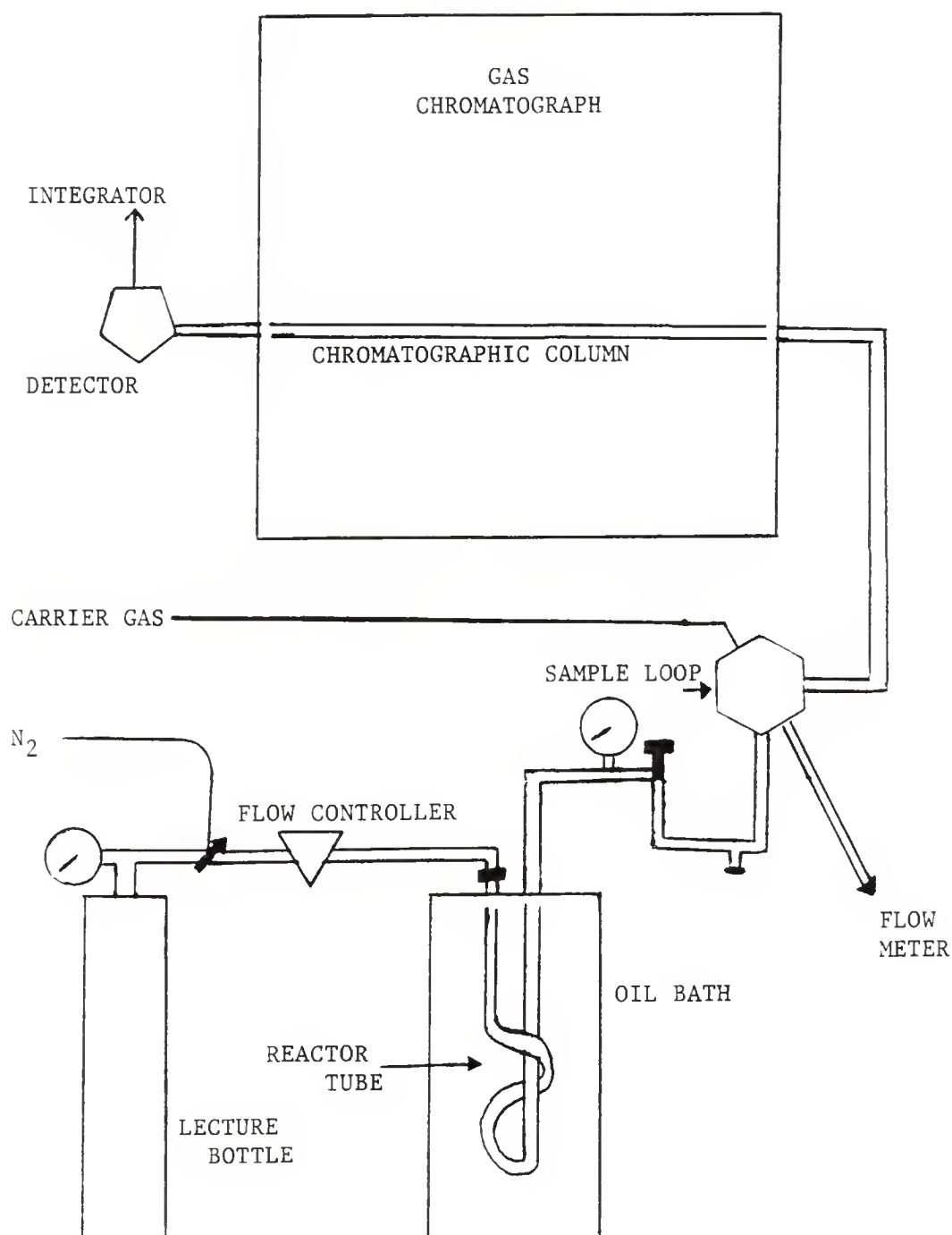


Figure 4-2. Gas flow reactor schematic.

loop which allows a 0.80 mL sample to be sent through a chromatographic column (diethylene glycol adipate, 60°C) in the GC equipped with a FID detector. The gas flow rate through the reactor tube is measured by a bubble flow meter at the end of the system.

Results and Discussion

The development and demonstration of this project is critically dependent upon the ability to achieve reaction quickly with moderate activity. The use of a catalyst under gas flow conditions necessitates this property. Many catalyst systems were initially studied in a closed reactor to determine if their activity was adequate for use in the flow reactor. Through these preliminary catalyst evaluations, it was determined that two catalysts were adequate for flow purposes. These are $\text{RhH(CO)(PPh}_3)_3$ and $\text{Rh(tfa)(PPh}_3)_3$. It was also determined that the mixture of support, catalyst, and excess ligand in the quantities described previously offered considerable reactivity over lower rhodium concentration mixtures.

Initial studies in the flow reactor presented many observations leading to the development of a more active reaction process. Included among the improvements made from these observations are slower flow rates, lower reaction temperatures, and most importantly pre-mixing of the gaseous substrates. In the later case, the activity obtained increased by five orders of magnitude! In hindsight, it indicates that with three individual substrate lines coming together, one of the gases, which has a slightly greater partial pressure than the other two, is

shutting off the other two gas flows. Therefore only one reactant is effectively coming in contact with the catalyst.

After the reaction had been demonstrated to occur at a considerable rate, the physical properties that affect reaction in the flow system are investigated to afford an optimized reaction process. The properties studied include temperature, pressure, gas flow rate, and substrate ratio. The catalyst RhH\SG is used to investigate these factors. Analysis of the gas stream after reaction is made by calculating the activity of a particular product. The activity, as defined in the equation below, is the number of moles of product produced in a given amount of time. Throughout the remainder of this section, all reported activity data, unless otherwise noted, will represent the activity achieved after production of n-butanal has maximized and leveled out.

$$\text{Activity} = (\text{moles}/0.8 \text{ mL})(\text{flow rate in mL/min})$$

The first of these properties studied is the influence of temperature upon reaction. The reaction is carried out at four temperatures to see the affect on both the selectivity and activity. At 50⁰C, little reactivity is observed. The selectivity of the reaction is difficult to determine due to the small amount of product which is produced. At a slightly elevated temperature, 65⁰C, the reaction proceeds at an increased rate. It is apparent from the analysis of the data that the quantity of n-butanal and isobutanal produced grows rapidly and after a period of time reaches a maximum and levels out.

The selectivity is determined to be 81.1% for the production of n-butanal relative to isobutanal. At a temperature of 80°C the reaction is observed to occur at a substantially greater rate than observed at 65°C; however the selectivity decreases slightly to 80.5%. At a temperature of 95°C, the reaction becomes erratic. Three different attempts to achieve reaction at this temperature produced three different sets of activity data. It appears from this information that even under slower flow rates, reaction is difficult to achieve at this temperature. The collected data indicates a substantial decrease in activity accompanied by a decrease in selectivity to 74%. In all cases, the amount of propylene converted to the linear and branched chain aldehydes is small (<1.4%), but with increasing temperature, it is shown to increase. The results of these experiments are summarized in table 4-1 and are shown graphically in figure 4-3. The activity data reported represents the activity obtained after the rate of production levels off. Typically, this is approximately thirty minutes.

After conducting the temperature dependence studies upon the reaction, it is apparent that a pattern develops in each system. The rate at which isobutanal is produced occurs at an increased rate relative to that of n-butanal as shown in figure 4-4. It reaches a maximum at an earlier time than the linear isomer and then levels off. Therefore the selectivity increases throughout the reaction with the maximum selectivity occurring after the production of n-butanal has maximized and leveled off. Data are shown in table 4-2.

The second property of the process to be investigated is the effect that the rate of gas flow has upon the reaction properties.

Table 4-1. Temperature effect upon propylene hydroformylation activity using RhH\SG.

<u>Temperature (°C)</u>	<u>Activity x10^{6a}</u>		<u>Selectivity (%)</u>	<u>Total Conversion (%)</u>
	<u>n-Butanal (moles/min)</u>	<u>Isobutanal (moles/min)</u>		
50	0.58	N.A.	---	<0.05
65	3.61	0.84	81.1%	0.35
80	11.4	2.76	80.5%	0.87
100 ^b	7.01	2.48	73.9%	1.35

^a Reactor conditions: 0.50g RhH\SG. Pressure is 13 psi using a (1:1:1) H₂, CO, and CH₃CH=CH₂ gas mixture. Rate of gas flow for various temperatures is 25 mL/min (50°C), 26 mL/min (65°C), 33 mL/min (80°C), 20 mL/min (100°C). Reaction time for various temperatures is 20 min. (50°C), 25 min. (65°C), 20 min. (80°C), 15 min. (95°C).

^b catalyst becomes less active and produces varying amounts of products.

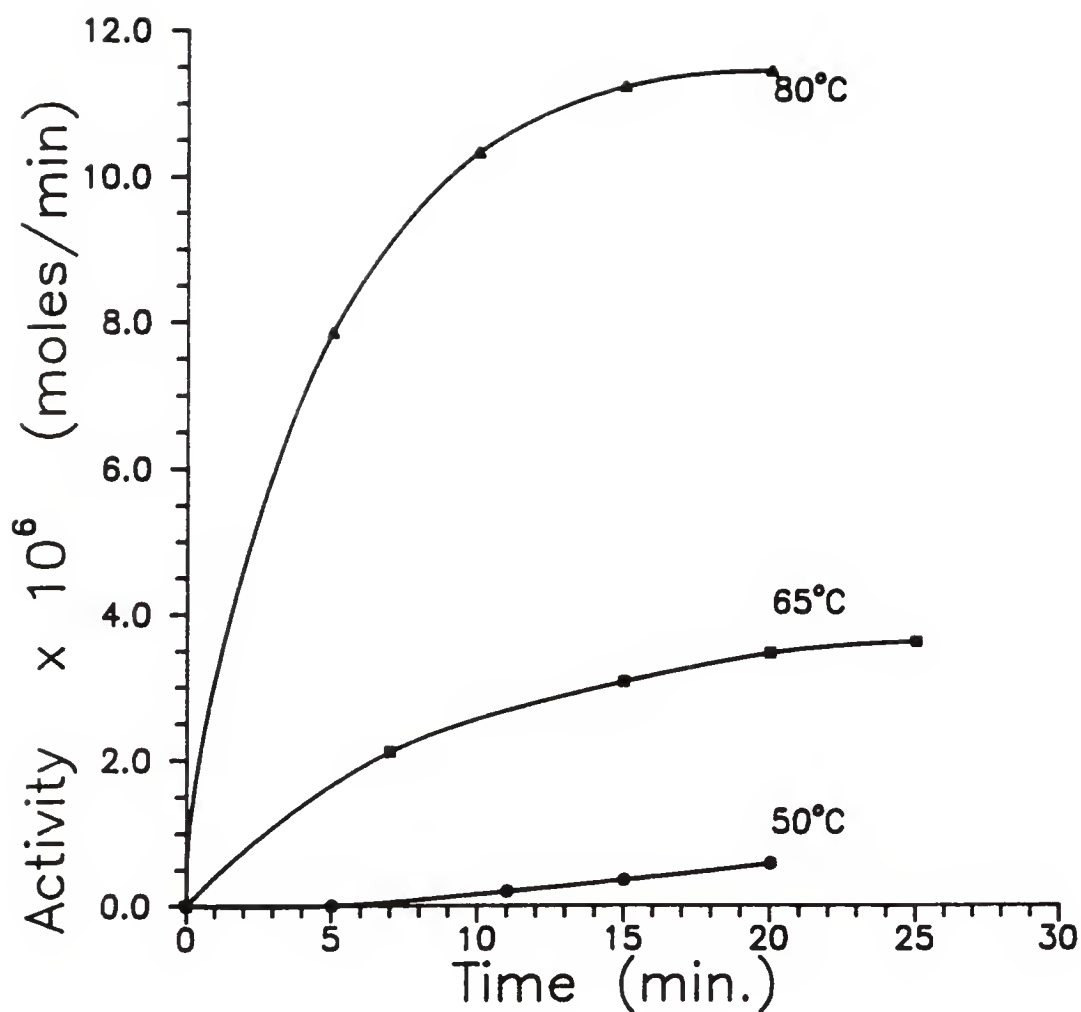


Figure 4-3.

n-Butanal activity as a function of temperature in the hydroformylation of propylene with RhH\SG.

Table 4-2. Selectivity as a function of time in the hydroformylation of propylene with RhH\SG.

Reaction Time (min)	<u>Activity $\times 10^6$^a</u>		Selectivity (%)	Total Conversion (%)
	<u>n-Butanal (moles/min)</u>	<u>Isobutanal (moles/min)</u>		
5	2.40	1.13	68.0	0.37
10	10.7	3.18	77.0	1.16
15	14.3	3.83	79.0	1.48
20	15.9	4.12	79.5	1.56
25	15.9	4.07	79.6	1.54

^a Reactor conditions: 0.50g RhH\SG. Temperature is 80°C. Pressure is 13 psi using a (1:1:1) H₂, CO, and CH₃CH=CH₂ gas mixture. Rate of gas flow is 12.5 mL/min.

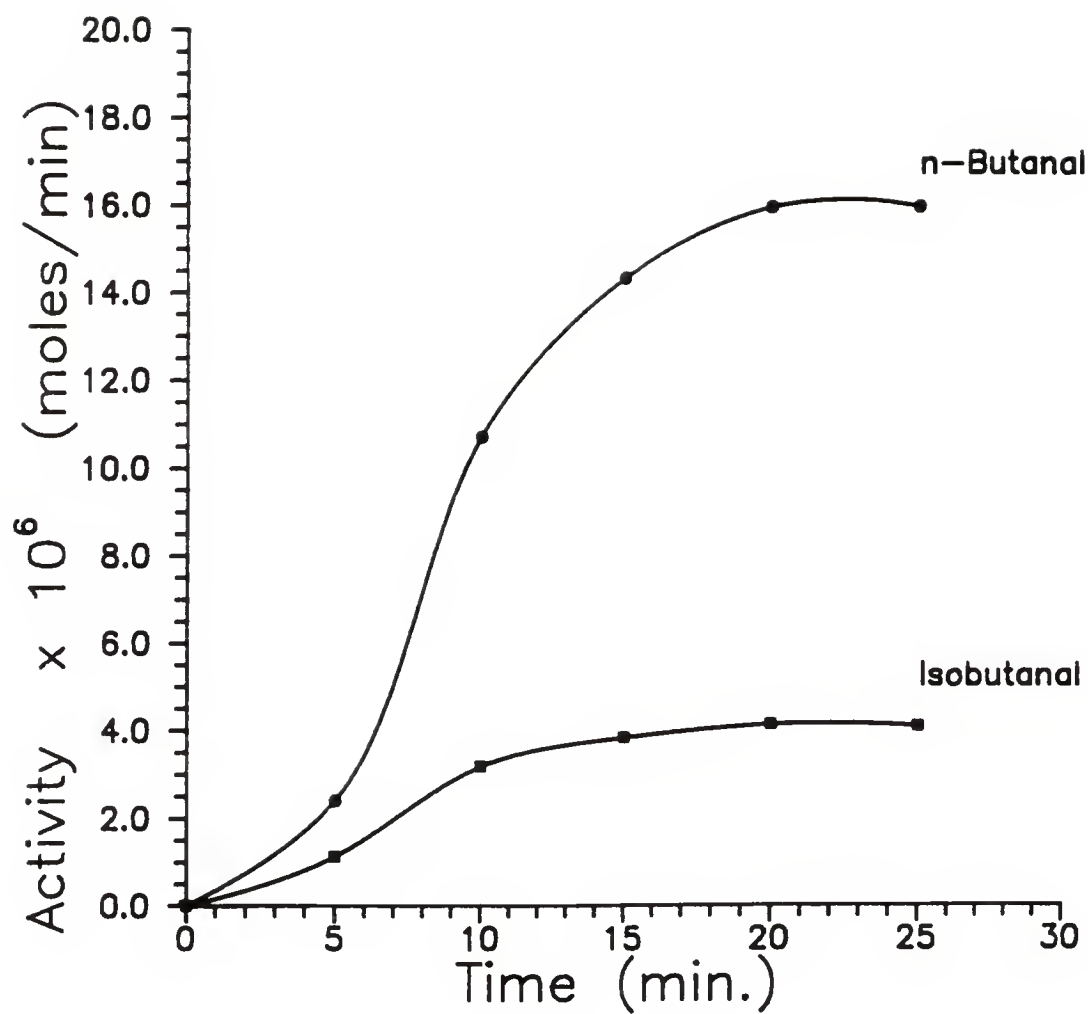


Figure 4-4.

Comparison of hydroformylation activity in the production of n-butanal and isobutanal with RhH\SG.

Again the catalyst system chosen to catalyze the reaction is RhH\SG. Based upon the reaction data, the maximum selectivity obtained occurs with the fastest flow rate. This advantage is offset by the fact that the smallest conversion of propylene also occurs with the fastest flow rate. An important observation from the flow rate data is that over the range of 7.7 mL/min to >30 mL/min, the activity that results reaches approximately the same magnitude. This is remarkable and indicates that under the slower flow rates, saturation of the catalyst environment with gaseous reactants is probably occurring, leading to improved reactivity. At the higher flow rates, a smaller fraction of the catalysts are interacting with the substrate. This, however, is offset by the increased quantities of reactants which are flowing through the reactor leading to similar activities as those reported for the slower flow rates.

The main difference observed using different flow rates is in the rate at which the maximum activity is obtained. This is shown graphically in figure 4-5. It is obvious that at extremely slow flow rates (2.0 mL/min), the greatest conversion occurs with the poorest selectivity. The activity obtained from the slower system is also substantially less than those of the higher flow rates. Given long enough reaction times, however, the activity should approach those of the faster flow rates. Data from the flow rate studies are presented in table 4-3.

The effect of increased pressure on the reaction under a continuous gas flow process is investigated. Once again, RhH\SG is the

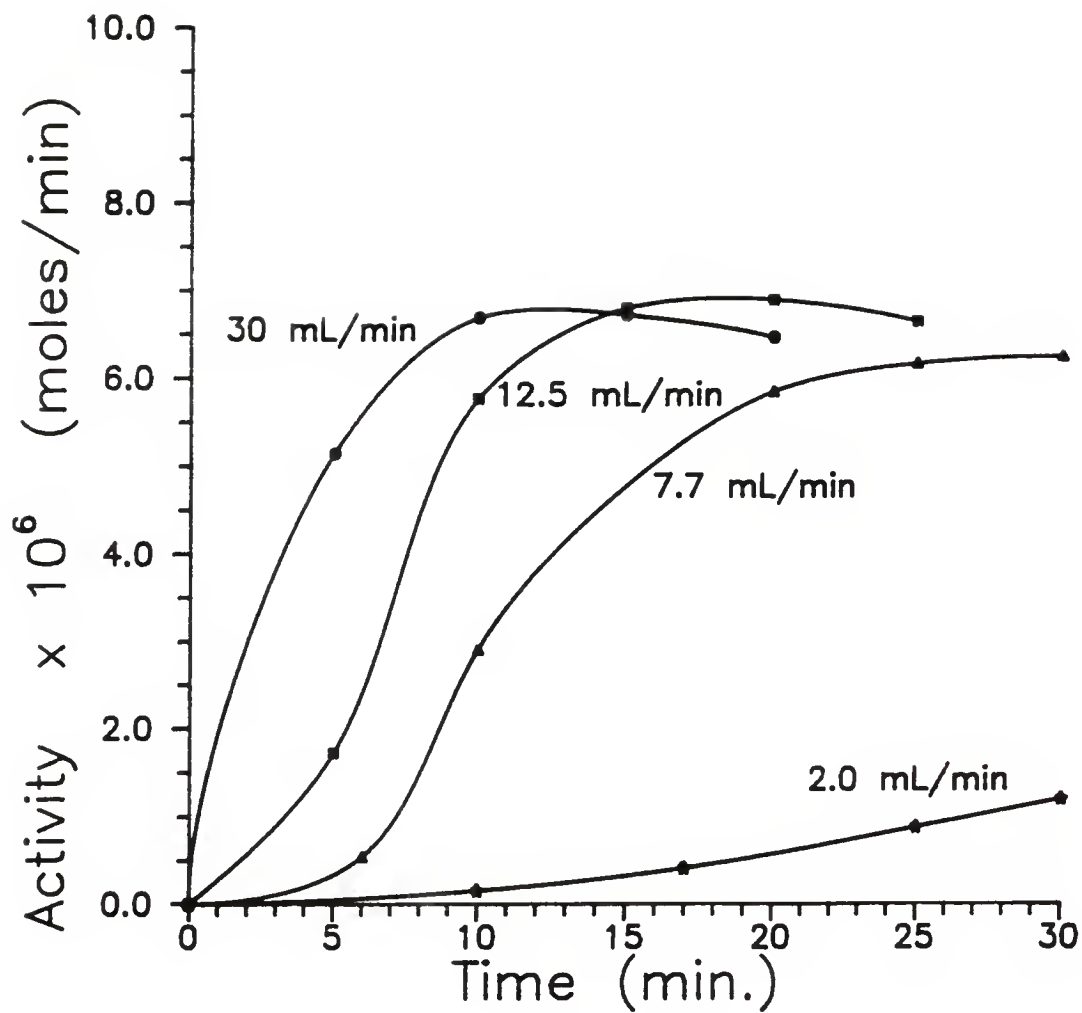


Figure 4-5. Effect of gas flow on the n-butanal activity in the hydroformylation of propylene with RhH\SG.

Table 4-3. Effect of gas flow on the hydroformylation of propylene with RhH\SG.

<u>Flow rate</u> <u>(mL/min)</u>	<u>Activity x10^{6a}</u>		<u>Selectivity</u> <u>(%)</u>	<u>Total</u> <u>Conversion</u> <u>(%)</u>
	<u>n-Butanal</u> <u>(moles/min)</u>	<u>Isobutanal</u> <u>(moles/min)</u>		
2.0	2.26	0.85	72.1	3.97
7.7	6.24	1.91	76.6	2.08
12.5	6.63	1.92	77.5	1.34
30.0	6.45	1.86	77.6	0.53

^a Reactor conditions: 0.50g RhH\SG. Pressure is 13 psi using a (1:1:1) H₂, CO, and CH₃CH=CH₂ gas mixture. Temperature is 80°C. Reaction time for various flow rates is 60 min. (2.0 mL/min), 30 min. (7.7 mL/min), 25 min. (12.5 mL/min), and 20 min. (30.0 mL/min).

catalyst system used for determining the affect of increased pressures. Reactions are conducted with 10, 20, and 45 psi pressure within the reactor tube. As expected, the most active system results from the highest gas pressure as shown graphically in figure 4-6. The increased activity is accompanied by an increase in the percent conversion of propylene and decreased selectivity. Data are reported in table 4-4.

The effect of the ratio of substrate gases utilized is also investigated. Ratios of 1:1:1, 3:1:1, and 1:3:1 hydrogen, carbon monoxide, and propylene are used for this purpose in conjunction with the RhH\SG catalyst. Slightly different flow rates in each reaction were used, however this should not affect the equilibrium activity obtained in any of the reactions. The total activity achieved in each case is small but indicates that an equivalent ratio of each gas (1:1:1) leads to the greatest activity (figure 4-7). The use of the higher quantity of hydrogen results in the most selective system. Data based on these results are shown in table 4-5.

Additional information is obtained from the above reactions. All optimization experiments described were achieved with the same catalyst, RhH\SG. After subjecting the catalyst to all these reported conditions, a gradual loss of activity is observed. It is important to note that all reactions used to investigate each reaction property were run consecutively with as nearly identical conditions as possible. This allows for accurate comparison of the individual reactions. However, comparison of an individual reaction from one investigative reaction series with that from another may result in slightly different

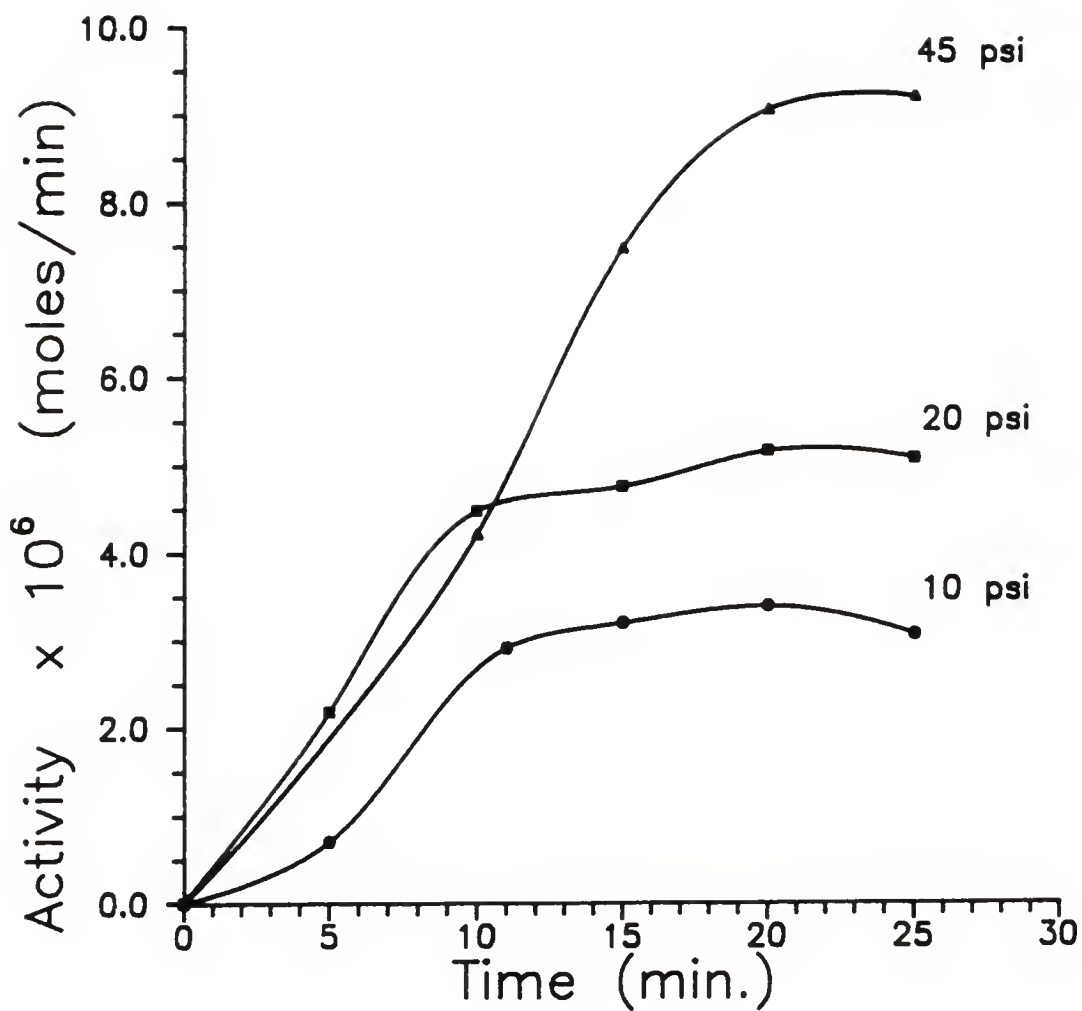


Figure 4-6.

Effect of gas pressure on the n-butanal activity in the hydroformylation of propylene with RhH\SG.

Table 4-4. Effect of gas pressure on the hydroformylation of propylene with RhH\SG.

Reactor Pressure (psi)	Activity $\times 10^6$ ^a		Selectivity (%)	Total Conversion (%)
	n-Butanal (moles/min)	Isobutanal (moles/min)		
10	3.06	0.90	77.3	0.49
20	5.07	1.46	77.6	0.72
45	9.19	3.18	74.3	1.29

^a Reactor conditions: 0.50g RhH\SG. Pressure is 13 psi using a (1:1:1) H₂, CO, and CH₃CH=CH₂ gas mixture. Temperature is 80°C. Rate of gas flow relative to various pressures is 16.0 mL/min (10 psi), 17.5 mL/min (20 psi), 19.5 mL/min (45 psi). Reaction time for various pressures is 25 min. (10 psi), 25 min. (20 psi), 25 min. (45 psi).

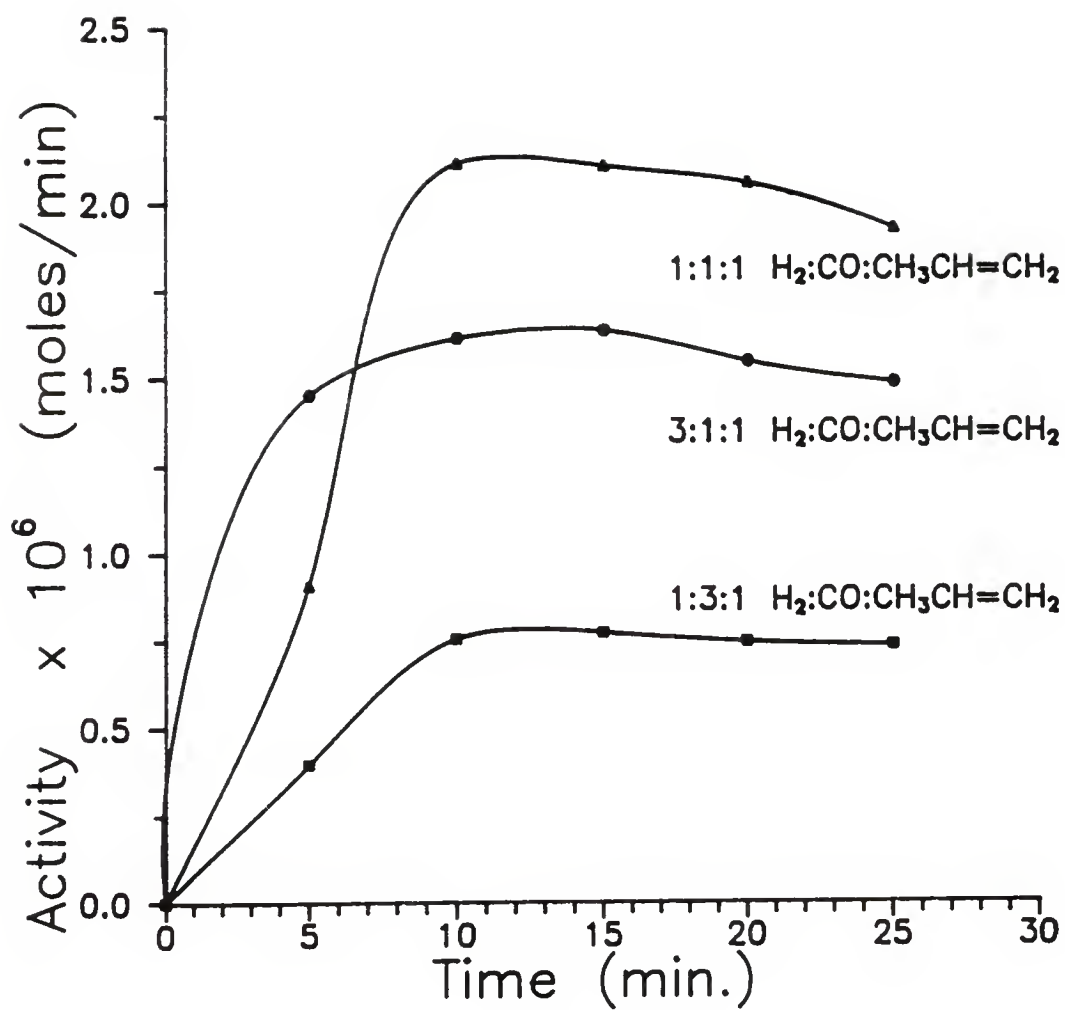


Figure 4-7.

Effect of gas ratios on the n-butanal activity in the hydroformylation of propylene with $\text{RhH}\backslash\text{SG}$.

Table 4-5. Effect of gas ratios on the hydroformylation of propylene with RhH\SG.

<u>H₂:CO:C₃H₆</u> <u>Ratio</u>	<u>Activity x10^{6a}</u>		<u>Selectivity</u> <u>(%)</u>	<u>Total</u> <u>Conversion</u> <u>(%)</u>
	<u>n-Butanal</u> <u>(moles/min)</u>	<u>Isobutanal</u> <u>(moles/min)</u>		
1:1:1	1.92	0.46	80.7	0.13
3:1:1	1.48	0.33	81.8	0.12
1:3:1	0.73	0.17	81.1	0.09

^a Reactor conditions: 0.50g RhH\SG. Pressure is 13 psi using a (1:1:1) H₂, CO, and CH₃CH=CH₂ gas mixture. Temperature is 80°C. Rate of gas flow for various gas mix ratios is 35.0 mL/min (1:1:1), 50.0 mL/min (3:1:1), 38.0 mL/min (1:3:1). Reaction time for various ratios is 25 min. (1:1:1), 25 min. (3:1:1), 25 min. (1:3:1).

activities or conversions. Based upon this observed gradual decrease in activity, all remaining experiments and catalyst evaluations are conducted with fresh (unused) catalysts.

The above studies allowed for the determination of the most optimum conditions of reaction. The most ideal reaction temperature is determined to be 80°C. The flow rate is not as critical since almost all give similar activities; however, flow rates of 7.5 to 20 mL give the best percent conversion of propylene. A pressure of 15 to 20 psi allows for moderate activity while maintaining a reasonable selectivity. Use of a 1:1:1 ratio of H₂:CO:propylene is determined to be the best for reactivity purposes. These reaction conditions are utilized in the following studies for the development of more active and selective catalysts.

Fresh RhH\SG catalyst was reran in the flow system using the determined optimum conditions. An equilibrated steady state activity of 15.9×10^{-6} moles/min is obtained for the production of n-butanal. A selectivity of 79.6% is also achieved. The analogous Rh(tfa)(PPh₃)₃ catalyst system, Rh(tfa)\SG, produces a greater selectivity (81.4%), but also results in considerably lower activity (1.93×10^{-6} moles/min) under identical conditions. This is shown graphically in figure 4-8.

The extremely high selectivity achieved in using polymer membranes (as shown in chapter 3) indicates that the polymer environment plays a large role in affecting the reaction properties. To test this theory, use of a similar environments in the flow reactor was tested. Reactions were ran at a temperature of 80°C using the previously determined optimum reaction conditions. The only reaction condition which

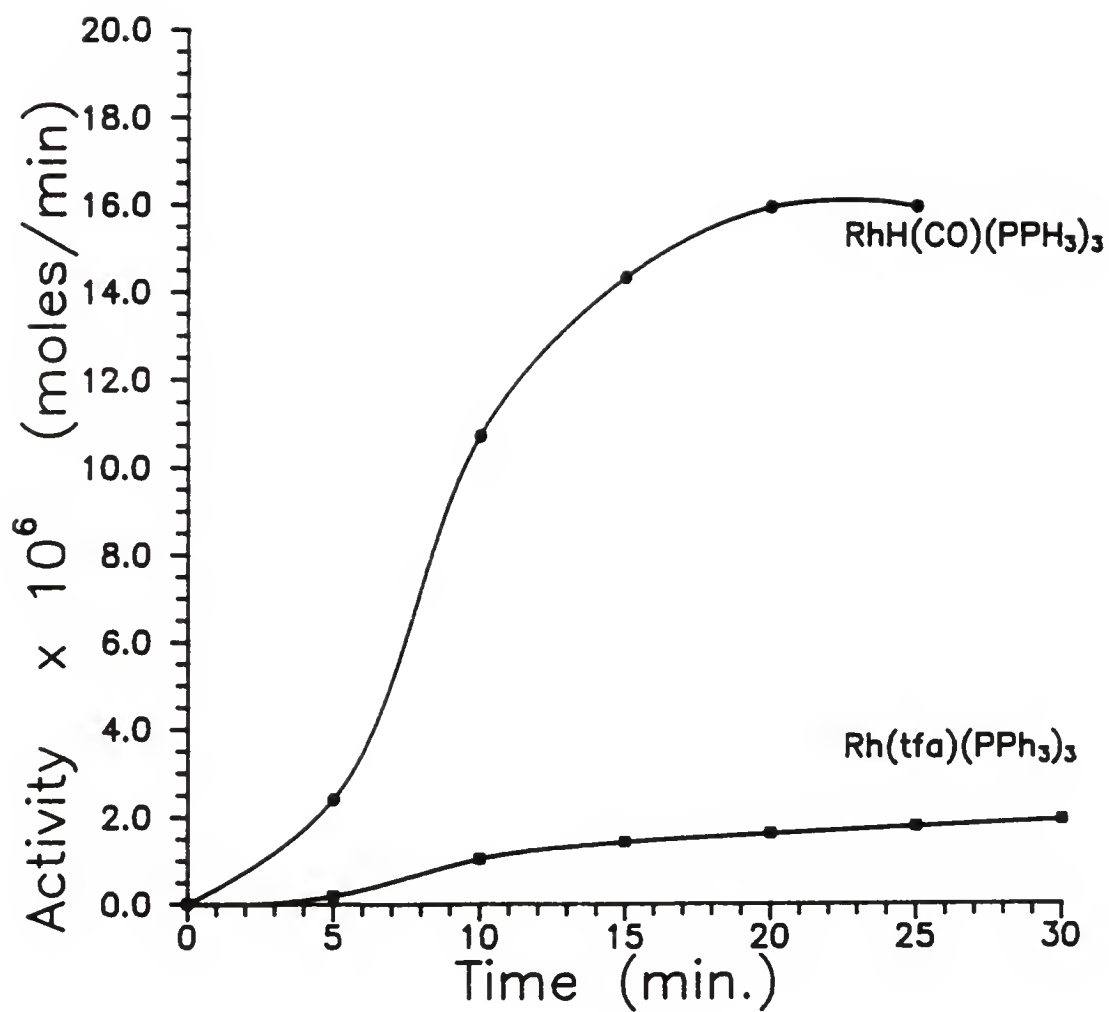


Figure 4-8. n-Butanal activity for $\text{RhH}\backslash\text{SG}$ and $\text{Rh(tfa)}\backslash\text{SG}$.

deviated from the optimum conditions was flow rate. In reactions where the catalyst activities were observed to be very low under moderate flow rates, the reactions were reran over longer periods of time using slower flow rates.

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$ on macroporous polystyrene, RhH/MPPS , was investigated. The results achieved are dramatic. The activity of the system is extremely small (0.33×10^{-6} for the production of n-butanal), however the selectivity observed is greater than 90%. Attempts to disperse $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ on ground-up poly(butyl methacrylate) results in the formation of a yellow solid which cannot be isolated for reaction purposes. Another polymer support investigated is Nafion.^{18,19} Use of this catalyst based system results in very little activity with high selectivity. The production of n-butanal occurs with an activity of 0.19×10^{-6} moles/min and >90% selectivity. Data for these systems are contained in table 4-6.

The reduced activity of the polymer supported systems is not unexpected. The filling of the reactor tube with a silica gel based catalyst results in a more densely packed volume. This results in increased substrate/catalyst interaction. Filling the reactor tube with the polymer based catalyst results in a more loosely packed volume in which pores and channels exist. This leads to decreased interaction between catalyst and substrate and decreased activity. The increased selectivity is noteworthy. It supports the theory that the polymer environment in both membrane and gas flow reactions alter the reaction properties. One property which the polymer may contribute is

Table 4-6. Catalyst comparison at 80°C.

<u>Catalyst</u>	<u>Activity x10^{6a}</u>		<u>Selectivity (%)</u>	<u>Total Conversion (%)</u>
	<u>n-Butanal (moles/min)</u>	<u>Isobutanal (moles/min)</u>		
RhH\SG	15.9	4.07	79.6	1.54
RhH\SG\PC	3.08	0.05	98.4	0.79
Rh(tfa)\SG	1.93	0.44	81.4	0.42
Rh(tfa)\SG\PC	0.02	0.00		0.01
RhH\MPPS	0.33	0.00	>90	0.16
RhH\MPPS\PC	0.35	0.00	>90	0.22
RhH\Nafion	0.19	0.00	>90	0.05

^a Reactor conditions: 0.50g catalyst. Pressure is 13 psi using a (1:1:1) H₂, CO, CH₃CH=CH₂ gas mixture. Temperature is 80°C. Flow rate for various reaction times is RhH\SG is 26.0 mL/min (25 min.) RhH\SG\PC is 8.0 mL/min (35 min.), Rh(tfa)\SG is 11.5 mL/min (30 min.), Rh(tfa)\SG\PC is 4.5 mL/min (20 min.), RhH\MPPS is 4.0 mL/min (30 min.), RhH\MPPS\PC is 3.4 mL/min (25 min.), RhH\Nafion is 7.3 mL/min (25 min.).

in its ability to act as a "sponge" in the reaction by soaking up the gaseous substrates and allowing reaction to occur.

This theory is further tested by attempting to mimic the polymer systems by coating the RhH\SG catalyst with an 8.0% loading of propylene carbonate. Propylene carbonate is a very polar solvent which has a large dielectric constant, $E = 69$, and a high boiling point, 242°C . It is nonvolatile under normal reaction conditions and no solvent evaporation is observed. The resulting propylene carbonate coated catalyst, RhH\SG\PC, results in reduced activity for n-butanal production (3.08×10^{-6} moles/min). The selectivity of the reaction, however, is observed to increase dramatically to 98.4%. This experimental result verifies the pronounced influence of the environment on this reaction.

Based upon this knowledge, Rh(tfa)\SG\PC was investigated. Using the previous reaction conditions, a reduced n-butanal activity (0.02×10^{-6} moles/min) is obtained. The selectivity again is increased but cannot be determined accurately. The formation of isobutanal is observed in such a small quantity that an accurate determination of the number of moles produced is not possible. Use of RhH\MPPS\PC yields similar results. Data from these reactions are listed in table 4-6.

The "sponge effect" which may be affecting reaction in the propylene carbonate added systems has also been investigated. This concept is tested by changing the reaction temperature. A higher reaction temperature, 100°C , has been shown to produce a decrease in the activity of the systems without the solvent coating. RhH\SG produces an activity of 7.01×10^{-6} moles/min in the formation of n-butanal and a

selectivity of 73.9%. In comparison, at 80°C the same system produces a n-butanal activity of 15.9×10^{-6} moles/min with a selectivity of 79.6%. Presumably, this occurs due to a minimized contact time between catalyst and substrates. The use of propylene carbonate may provide increased contact time between the catalyst and substrate by acting as a sponge.

The use of RhH\MPPS\PC at 100°C results in increased activity (0.79×10^{-6} moles/min) relative to its analogous 80°C experiment (0.33×10^{-6} moles/min) without propylene carbonate. Accompanying the increased activity is increased selectivity. No isobutyraldehyde is observed in the system. If it is present, there is too little of an amount to detect. The most dramatic results are achieved in the RhH\SG\PC. Again for reference purposes, RhH\SG has an activity of 7.01×10^{-6} moles/min in the formation of n-butanal and a selectivity of 73.9%. RhH\SG\PC produces an incredible increase in activity and selectivity. The production of n-butanal is obtained with an activity of 36.4×10^{-6} moles/min and a remarkable 95.7% selectivity. Data are summarized in table 4-7 and presented graphically in figure 4-9. The activity generated in this system produces about 45 turnovers of n-butanal in one hour with a space velocity of 1370 hr^{-1} . Equally as important is the observation that greater than 4% of the propylene is converted to n-butanal. This is achieved in one pass through the reactor tube. On a commercial scale, the reaction engineering could be altered to produce much higher conversions.

In conclusion, it has been demonstrated that the production of n-butanal and isobutanal can be achieved in a gas flow reactor using supported rhodium catalysts. It has also been shown that increased

Table 4-7. Catalyst comparison at 100°C.

<u>Catalyst</u>	<u>Activity x10^{6a}</u>		<u>Selectivity (%)</u>	<u>Total Conversion (%)</u>
	<u>n-Butanal (moles/min)</u>	<u>Isobutanal (moles/min)</u>		
Rh(tfa)\SG	1.39	0.47	74.8	0.39
RhH\MPPS\PC	0.79	0.00	>90	0.17
RhH\SG	7.01	2.48	73.9	1.35
RhH\SG\PC	36.4	1.64	95.7	4.1

^a Reactor conditions: 0.50g catalyst. Pressure is 13 psi using a (1:1:1) H₂, CO, and CH₃CH=CH₂ gas mixture. Temperature is 100°C. Flow rate for various reaction times is Rh(tfa)\SG is 9.4 mL/min (30 min.), RhH\MPPS\PC is 9.5 mL/min (25 min.), RhH\SG is 11.0 mL/min (15 min.), RhH\SG\PC is 18.0 mL/min (60 min.).

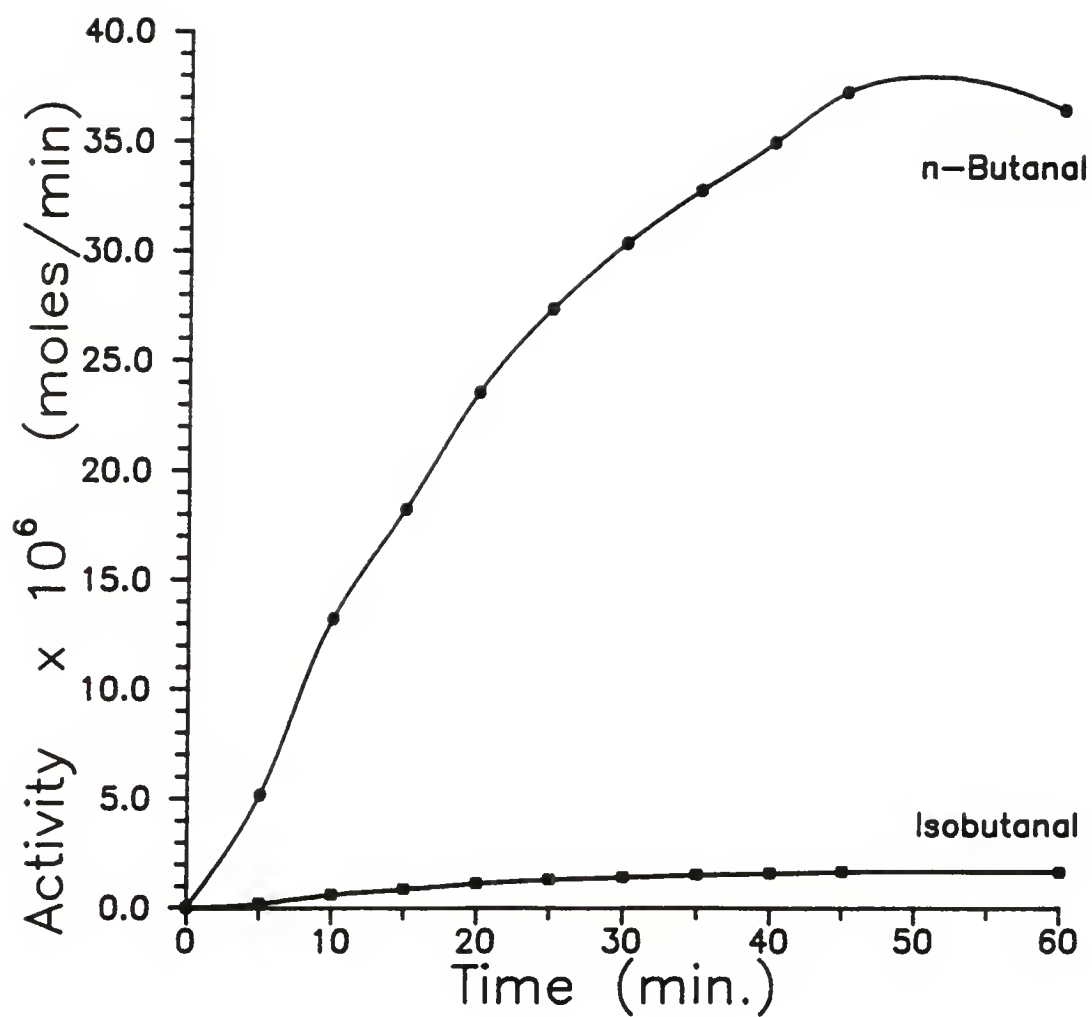


Figure 4-9.

Butanal activity as a function of time in the hydroformylation of propylene with RhH\SG\PC at 100°C.

selectivity occurs with polymer supported catalysts relative to silica gel supported catalysts. The use of a nonvolatile polar solvent for coating purposes results in a substantially increased selectivity and provides substrate saturation of the catalyst environment. This results in increased activity even using the less favorable conditions (higher temperatures) of the uncoated systems. This verifies the pronounced influence that the polymer has in the previously demonstrated membrane reactions (chapter 3).

CHAPTER V SUMMARY

This research focuses on combining transition metal reaction chemistry and membrane technology. Specifically, this work involves three regions of this hybrid area. The first is concerned with the ability of a transition metal complex to affect the permeation properties of a polymer membrane. Investigation into this area has resulted in the development of a procedure for accomplishing facilitated transport of oxygen. The permeability coefficient for nitrogen in the sample membrane is used as an internal standard and is used to determine the quantity of oxygen which permeates via a facilitated transport mechanism. This study has demonstrated that supported cobalt complexes incorporated into a polystyrene membrane enhance the permeation of oxygen.

The second area of research investigates the use of a polymer environment as the medium for chemical reaction. The concept of membranes utilized for reaction purposes continues to be of industrial significance. This stems from their ability to serve a dual purpose by achieving reaction and then functioning as a separation unit. The feasibility of this process is realized by the facilitation of both hydroformylation and oxidation reactions in polystyrene, poly(butyl methacrylate), and silicone gum rubber media. Versatility of membrane reactors is evidenced by alkyl sulfide oxidations and hydrogen peroxide

formation in similar polymer membranes. The selectivity obtained in the hydroformylation of propylene to n-butanal is encouraging. The activity of these systems is low, but improved engineering in conjunction with optimization of reaction conditions should provide increased activity.

Lastly, the extension of membrane reactors to a continuous flow, gas phase hydroformylation reaction process has been achieved with remarkable success. This process utilizes the membrane reactor concept by coating the catalyst system with viscous materials or films. The use of a heterogeneous catalyst based system yields substantially increased activity while maintaining the high degree of selectivity associated with polymer membrane reactors. This is accomplished with solid supported rhodium catalysts which are coated with a viscous material, propylene carbonate. These catalysts are capable of producing linear aldehyde selectivities of greater than twenty-two to one. Use of these catalyst systems produces forty-five turnovers in one hour. Development of this process is continuing to be investigated for improved reaction properties.

APPENDIX A COMPUTER PROGRAM FOR OXYGEN ENRICHMENT ANALYSIS

The following program was co-written with Ngai Wong. It allows for the determination of both oxygen and nitrogen permeability coefficients using either inputted partial pressures or measured total pressure and oxygen percentages. The program will calculate the separation factor of a membrane as well as determine the enrichment from the membrane that occurs by a facilitated transport mechanism.


```

DEF FNUCASE$(X$)
LENGTH=LEN(X$)
IF LENGTH=0 THEN FNUCASE$="":EXIT DEF
FOR I=1 TO LENGTH
CH=ASC(MID$(X$,I,1))
IF CH>96 AND CH<127 THEN
MID$(X$,I,1)=CHR$(CH-32)
END IF
NEXT I
FNUCASE$=X$
END DEF
DEF FNNUM$(X)
X$ = STR$(X)
LENGTH = LEN(X$)
IF LEFT$(X$,1) <> "-" THEN LENGTH = LENGTH - 1
FNNUM$ = RIGHT$(X$,LENGTH)
END DEF
DEFINT I
DIM SHARED RT(15),O2A(15),PB(15),O2B(15),FLUX(15),PO2(15),PN2(15)
DIM SHARED LNPO2(15),LNPN2(15),O2S(15),O2R(15),LP02B(15),POB(15)
DIM SHARED ENR(15),XIN(3,15),YIN(3,15),IX(3,15),IY(3,15),RES(3,15)
DIM SHARED ILO(3),IHI(3),NP(3)
10 PRINT " IS THE O2 ENRICHMENT DATA IN A DATA FILE? Y/N "
999 ANS$=FNUCASE$(INKEY$)
IF ANS$="" GOTO 999
IF ANS$="N" GOTO 20
IF ANS$="Y" GOTO 30
GOTO 10
20 PRINT:PRINT "Is your data in partial pressures? Y/N"
998 ANS$ = FNUCASE$(INKEY$)
IF ANS$="" GOTO 998
IF ANS$ = "Y" GOTO 25
IF ANS$ <> "N" GOTO 20
INPUT " HOW MANY DATA POINTS? MAX=15 ";N:PRINT
PRINT " FOR RETENTION TIME = 0, ENTER 0 FOR O2S AND 1 FOR PB":PRINT
PRINT " ENTER RUN TIME, RT; O2 IN AIR, O2A; O2 AFTER SEP., O2S"
PRINT " PRESS IN BOT CHAMBER, PB":PRINT
FOR I = 1 TO N
PRINT " RT, O2A, O2S, AND PB FOR POINT "I
INPUT RT(I),O2A(I),O2S(I),PB(I)
NEXT I
40 PRINT " DATA ENTERED IS RT, O2A, O2S, AND PB FOR "N" POINTS"
50 PRINT
FOR I = 1 TO N
PRINT I)"",RT(I),O2A(I),O2S(I),PB(I)
NEXT I
60 PRINT " A - ADD A POINT"
PRINT " C - CHANGE A POINT"
PRINT " D - DELETE A POINT"
PRINT " N - DO NOTHING"
997 ANS$=FNUCASE$(INKEY$)
IF ANS$="" GOTO 997
IF ANS$="N" GOTO 70
IF ANS$="A" GOTO 80
IF ANS$="C" GOTO 90
IF ANS$="D" GOTO 100
GOTO 60
80 IF N<15 GOTO 110
PRINT " MAX NUMBER OF POINTS EXCEEDED! ": GOTO 50
110 N=N+1
PRINT " ENTER RT, O2A,O2S, AND PB FOR NEW POINT"
INPUT RT(N),O2A(N),O2S(N),PB(N)
GOTO 50
90 INPUT " WHAT POINT DO YOU WISH TO CHANGE";J
IF J>N GOTO 50
IF J<1 GOTO 50
PRINT " WHAT ARE THE NEW VALUES OF RT, O2A, O2S, PB FOR POINT "J
INPUT RT(J),O2A(J),O2S(J),PB(J)
GOTO 50

```

```

100 INPUT " WHAT POINT DO YOU WISH TO DELETE";J
    IF J>N GOTO 50
    IF J<1 GOTO 50
    N=N-1
    FOR I = J TO N
        RT(I)=RT(I+1):O2A(I)=O2A(I+1):O2S(I)=O2S(I+1):PB(I)=PB(I+1):NEXT I
    GOTO 50
25 INPUT " HOW MANY DATA POINTS? MAX=15 ";N:PRINT
    PRINT " FOR RETENTION TIME = 0, ENTER 0 FOR PO2 AND PN2":PRINT
    PRINT " ENTER RUN TIME, RT; O2 IN AIR, O2A; PART. PRESS. OF O2, PO2;"
    PRINT " PARTIAL PRESSURE OF N2, PN2":PRINT
    FORM$ = "PARTIAL"
    FOR I = 1 TO N
        PRINT " RT, O2A, PO2, AND PN2 FOR POINT "I
        INPUT RT(I),O2A(I),PO2(I),PN2(I)
    NEXT I
41 PRINT " DATA ENTERED IS RT, O2A, PO2, AND PN2 FOR "N" POINTS"
51 PRINT
    FOR I = 1 TO N
        PRINT I)"",RT(I),O2A(I),PO2(I),PN2(I)
    NEXT I
61 PRINT " A - ADD A POINT"
    PRINT " C - CHANGE A POINT"
    PRINT " D - DELETE A POINT"
    PRINT " N - DO NOTHING"
996 ANS$=FNUCASE$(INKEY$)
    IF ANS$="" GOTO 996
    IF ANS$="N" GOTO 70
    IF ANS$="A" GOTO 81
    IF ANS$="C" GOTO 91
    IF ANS$="D" GOTO 101
    GOTO 61
81 IF N<15 GOTO 111
    PRINT " MAX NUMBER OF POINTS EXCEEDED! ": GOTO 51
111 N=N+1
    PRINT " ENTER RT, O2A, PO2, AND PN2 FOR NEW POINT"
    INPUT RT(N),O2A(N),PO2(N),PN2(N)
    GOTO 51
91 INPUT " WHAT POINT DO YOU WISH TO CHANGE";J
    IF J>N GOTO 51
    IF J<1 GOTO 51
    PRINT " WHAT ARE THE NEW VALUES OF RT, O2A, PO2, PN2 FOR POINT "J
    INPUT RT(J),O2A(J),PO2(J),PN2(J)
    GOTO 51
101 INPUT " WHAT POINT DO YOU WISH TO DELETE";J
    IF J>N GOTO 51
    IF J<1 GOTO 51
    N=N-1
    FOR I = J TO N
        RT(I)=RT(I+1):O2A(I)=O2A(I+1):PO2(I)=PO2(I+1):PN2(I)=PN2(I+1):NEXT I
    GOTO 51
70 GOSUB 300
    FOR I = 1 TO N
        IF RT(I)=0 THEN PO2(I) = 0.22
        IF RT(I)=0 THEN PN2(I) = 0.78
        IF FORM$ = "PARTIAL" GOTO 121
        IF RT(I)=0 THEN O2BD(I)=O2A(I)
        IF RT(I)=0 GOTO 120
        O2BD(I)= (760*O2S(I)-(760-PB(I))*O2A(I))/PB(I)
120 O2R(I)=O2BD(I)-O2A(I)
        IF RT(I)=0 THEN FLUX(I)=0 ELSE FLUX(I)=PB(I)/RT(I)
        PO2(I)=O2BD(I)*PB(I)/100
        PN2(I)=PB(I)-PO2(I)
121 LNPO2(I)=LOG(((760*O2A(I))/100)-PO2(I))
        LNP2(I)=LOG(((760*(100-O2A(I))/100)-PN2(I))
    NEXT I
    IF FORM$ = "PARTIAL" GOTO 145
    PRINT " CALCULATED DATA - O2BD = O2 BEFORE DILUTION"
    PRINT " O2R = O2 ENRICHMENT"

```

```

PRINT "                                FLUX = O2 FLUX"
PRINT "                                PO2  = PARTIAL PRESSURE OF O2"
PRINT "                                PN2  = PARTIAL PRESSURE OF N2"
PRINT " HIT ANY KEY TO CONTINUE "
995 AAS$=INKEY$
IF AAS$="" GOTO 995
CLS:PRINT " CALCULATED DATA AS FOLLOWS RT, O2BD, O2R, AND FLUX":PRINT
FOR I=1 TO N
PRINT I)"",RT(I),O2BD(I),O2R(I),FLUX(I)
NEXT I
PRINT "HIT ANY KEY TO CONTINUE"
994 ANS$=INKEY$
IF ANS$="" GOTO 994
PRINT " DO YOU WANT A HARDCOPY OF THIS? Y/N"
880 ANS$=FNUCASE$(INKEY$)
IF ANS$ = "" GOTO 880
IF ANS$ <> "Y" GOTO 140
OPEN "LPT1:" FOR OUTPUT AS #1
PRINT #1, " CALCULATED DATA AS FOLLOWS RT, O2BD, O2R, AND FLUX":PRINT #1,""
FOR I = 1 TO N
PRINT #1, I)"",RT(I),O2BD(I),O2R(I),FLUX(I)
NEXT I
PRINT #1,""
CLOSE #1
CLS:GOTO 140
130 PRINT
140 PRINT " CALCULATED DATA AS FOLLOWS RT, PB, PO2, AND PN2":PRINT
FOR I = 1 TO N
PRINT I)"",RT(I),PB(I),PO2(I),PN2(I)
NEXT I
PRINT:PRINT "HIT ANY KEY TO CONTINUE"
993 ANS$=INKEY$
IF ANS$="" GOTO 993
PRINT "DO YOU WANT A HARDCOPY OF THIS? Y/N"
879 ANS$=FNUCASE$(INKEY$)
IF ANS$="" GOTO 879
IF ANS$<>"Y" GOTO 145
OPEN "LPT1:" FOR OUTPUT AS #1
PRINT #1," CALCULATED DATA AS FOLLOWS RT, PB, PO2, AND PN2":PRINT #1,""
FOR I = 1 TO N
PRINT #1,I)"",RT(I),PB(I),PO2(I),PN2(I)
NEXT I
PRINT #1,""
CLOSE #1
145 FOR I = 1 TO N
XIN(1,I) = RT(I)
NEXT I
NSET = I
FOR I = 1 TO 2
FOR J = 1 TO N
IF I = 1 THEN YIN(1,J) = LNPO2(J) ELSE YIN(1,J) = LNPN2(J)
NEXT J
CALL LEAST(N,M,B,SDM,SDB,RES,RESVAR,SE,NSET)
IF I = 1 THEN O2SLOP=M ELSE N2SLOP=M
IF I = 1 THEN BINTC = B
IF I = 2 GOTO 165
PRINT:PRINT "Slope of Ln O2 vs reaction time is "O2SLOP
GOTO 166
165 PRINT:PRINT "Slope of Ln N2 vs reaction time is "N2SLOP
166 PRINT "Intercept for this plot is "B
PRINT "Standard deviation of slope is "SDM
PRINT "Standard deviation of intercept is "SDB
PRINT "Residual variance is "RESVAR
PRINT "Standard estimated error is "SE
PRINT:PRINT
992 ANS$=INKEY$
IF ANS$="" GOTO 992
PRINT "DO YOU WANT A HARDCOPY OF THIS? Y/N"
878 ANS$=FNUCASE$(INKEY$)

```

```

IF ANS$="" GOTO 878
IF ANS$<> "Y" GOTO 877
OPEN "LPT1:" FOR OUTPUT AS #1
IF I = 2 GOTO 876
PRINT #1,"Slope of Ln O2 vs reaction time is "O2SLOP
GOTO 875
876 PRINT #1,"Slope of Ln N2 vs reaction time is "N2SLOP
875 PRINT #1,"Intercept for this plot is "B
PRINT #1,"Standard deviation of slope is "SOM
PRINT #1,"Standard deviation of intercept is "SDB
PRINT #1,"Residual variance is "RESVAR
PRINT #1,"Standard estimated error is "SE
PRINT #1,""
CLOSE #1
877 PRINT:PRINT "The following plot routines will use points."
PRINT "Please specify symbols for points."
991 ANS$=INKEY$
IF ANS$="" GOTO 991
CALL SETUP(TITLE$,XLA$,YLA$,MAJX,MINX,YMAJ,YMIN,POIN$)
CALL CONVERT(PXL,PXH,PYL,PYH,NSET,N)
CLS
CALL GMODE
CALL CLRSCR
CALL LAB(TITLE$,XLA$,YLA$)
CALL AXIS(MAJX,MINX,YMAJ,YMIN)
CALL STRAIGHT(PXL,PXH,M,B,PYL,PYH)
CALL DOT(POIN$,NSET,N)
CALL SCALE(PXL,PXH,MAJX,PYL,PYH,YMAJ)
990 ANS$=INKEY$
IF ANS$="" GOTO 990
CALL TMODE
NEXT I
170 PRINT " DO YOU WISH TO CALCULATE ALPHA? Y/N "
989 ANS$=FNUCASE$(INKEY$)
IF ANS$="" GOTO 989
IF ANS$="N" GOTO 180
IF ANS$="Y" GOTO 190
GOTO 170
190 INPUT " WHAT IS THE FILM THICKNESS"; THIC
INPUT " WHAT IS THE FILM AREA"; AREA
INPUT " WHAT IS THE TEMPERATURE"; TEMP
INPUT " WHAT IS THE CELL VOLUME"; VOL
GOTO 200
210 PCO2=-O2SLOP*22414*VOL*THIC/(TEMP*AREA*3600*6.24E5)
PCN2=-N2SLOP*22414*VOL*THIC/(TEMP*AREA*3600*6.24E5)
ALPHA=PCO2/PCN2
CLS: PRINT " THE FILM THICKNESS IS "THIC
PRINT " THE FILM AREA IS "AREA
PRINT " THE TEMPERATURE IS "TEMP
PRINT " THE CELL VOLUME IS "VOL
PRINT:PRINT " THE PERMEABILITY COEFF FOR O2 IS "PCO2
PRINT " THE PERMEABILITY COEFF FOR N2 IS "PCN2
PRINT " THE SEPERATION FACTOR IS "ALPHA
PRINT:PRINT:PRINT:PRINT " HIT ANY KEY TO CONTINUE "
988 AA$=INKEY$
IF AA$="" GOTO 988
PRINT "DO YOU WANT A HARDCOPY OF THIS? Y/N"
874 ANS$=FNUCASE$(INKEY$)
IF ANS$="" GOTO 874
IF ANS$<>"Y" GOTO 180
OPEN "LPT1:" FOR OUTPUT AS #1
PRINT #1," THE FILM THICKNESS IS "THIC
PRINT #1," THE FILM AREA IS "AREA
PRINT #1," THE TEMPERATURE IS "TEMP
PRINT #1,"":PRINT #1," THE PERMEABILITY CEFF FOR O2 IS "PCO2
PRINT #1," THE PERMEABILITY COEFF FOR N2 IS "PCN2
PRINT #1," THE SEPERATION FACTOR IS "ALPHA
PRINT #1,""
CLOSE #1

```

```

GOTO 180
200 PRINT:PRINT " THE FILM THICKNESS IS "THIC
PRINT " THE FILM AREA IS "AREA
PRINT " THE TEMPERATURE IS "TEMP
PRINT " THE CELL VOLUME IS "VOL
220 PRINT:PRINT " DO YOU WANT TO CHANGE ANYTHING? Y/N "
987 ANS$=FNUCASE$(INKEY$)
IF ANS$="" GOTO 987
IF ANS$="N" GOTO 210
IF ANS$="Y" GOTO 230
GOTO 220
230 PRINT " WHAT WOULD YOU LIKE TO CHANGE? L, A, T, OR V "
986 ANS$=FNUCASE$(INKEY$)
IF ANS$="" GOTO 986
IF ANS$="L" GOTO 240
IF ANS$="A" GOTO 250
IF ANS$="T" GOTO 260
IF ANS$="V" GOTO 270
GOTO 200
240 INPUT " WHAT IS THE FILM THICKNESS";THIC
GOTO 200
250 INPUT " WHAT IS THE FILM AREA";AREA
GOTO 200
260 INPUT " WHAT IS THE TEMPERATURE";TEMP
GOTO 200
270 INPUT " WHAT IS THE CELL VOLUME";VOL
GOTO 200
290 END
180 PRINT:PRINT " DO YOU WANT TO RUN THIS DATA AGAIN? Y/N "
985 ANS$=FNUCASE$(INKEY$)
IF ANS$="" GOTO 985
IF ANS$="N" GOTO 330
IF ANS$="Y" GOTO 40
GOTO 180
30 PRINT:INPUT " WHAT IS THE FILENAME OF THE DATA? (FILENAME.EXT) ";A$
OPEN A$ FOR INPUT AS #5
INPUT #5, N
INPUT #5, FORM$
FOR I = 1 TO N
IF FORM$ <> "PARTIAL" THEN INPUT #5,RT(I),O2A(I),O2S(I),PB(I)
IF FORM$ = "PARTIAL" THEN INPUT #5,RT(I),O2A(I),PO2(I),PN2(I)
NEXT I
CLOSE #5
IF FORM$ = "PARTIAL" THEN GOTO 41 ELSE GOTO 40
300 PRINT:PRINT " DO YOU WISH TO SAVE THIS DATA? Y/N "
984 ANS$=FNUCASE$(INKEY$)
IF ANS$="" GOTO 984
IF ANS$="N" GOTO 310
IF ANS$="Y" GOTO 320
GOTO 300
320 PRINT:INPUT " FILENAME YOU WISH TO SAVE DATA UNDER (FILENAME.EXT)";A$
OPEN A$ FOR OUTPUT AS #4
PRINT #4, N
PRINT #4, FORM$
FOR I = 1 TO N
IF FORM$ <> "PARTIAL" THEN PRINT #4,RT(I),O2A(I),O2S(I),PB(I)
IF FORM$ = "PARTIAL" THEN PRINT #4,RT(I),O2A(I),PO2(I),PN2(I)
NEXT I
CLOSE #4
PRINT:PRINT " DATA HAS BEEN SAVED IN FILE : "A$:PRINT
310 RETURN
330 PRINT:PRINT "Do you want to calculate the reference data? Y/N"
983 ANS$ = FNUCASE$(INKEY$)
IF ANS$="" GOTO 983
IF ANS$ = "N" GOTO 301
IF ANS$ <> "Y" GOTO 330
PRINT:INPUT "What value of reference ALPHA do you want";ALPHA2
PCO2B = ALPHA2 * PCN2
BSLOP = -1 * PCO2B * TEMP * AREA * 10022.4 / (VOL * THIC / 10)

```

```

FOR I = 1 TO N
  LPO2B(I) = BSLOP * RT(I) + BINTC
  POB(I) = O2A(I) * 7.60 - EXP(LPO2B(I))
  IF RT(I)=0 THEN POB(I)=.22
  ENR(I) = PO2(I) - POB(I)
NEXT I
PRINT:PRINT "Permeability of O2 blank is "PCO2B
PRINT "Blank slope is "BSLOP
PRINT:PRINT "Run time      PO2      POB      Enrich":PRINT
FOR I = 1 TO N
  PRINT RT(I),PO2(I),POB(I),ENR(I)
NEXT I
PRINT:PRINT "Hit any key to continue."
982 ANS$ = INKEY$
  IF ANS$="" GOTO 982
  PRINT "DO YOU WANT A HARDCOPY OF THIS? Y/N"
873 ANS$=FNUCASE$(INKEY$)
  IF ANS$="" GOTO 873
  IF ANS$<>"Y" GOTO 872
  OPEN "LPT1:" FOR OUTPUT AS #1
  PRINT #1," Permeability of O2 blank is "PCO2B
  PRINT #1," Blank slope is "BSLOP
  PRINT #1,"":PRINT #1,"Run time      PO2      POB      Enrich":PRINT #1,""
  FOR I =1 TO N
    PRINT #1,RT(I),PO2(I),POB(I),ENR(I)
  NEXT I
  PRINT #1,""
  CLOSE #1
872 PRINT:PRINT "Run time      Ln PO2B":PRINT
  FOR I = 1 TO N
    PRINT RT(I),LPO2B(I)
  NEXT I
  PRINT:PRINT "Hit any key to continue."
981 ANS$ = INKEY$
  IF ANS$="" GOTO 981
  PRINT "DO YOU WANT A HARDCOPY OF THIS? Y/N"
871 ANS$=FNUCASE$(INKEY$)
  IF ANS$="" GOTO 871
  IF ANS$<>"Y" GOTO 340
  OPEN "LPT1:" FOR OUTPUT AS #1
  PRINT #1," Run time      Ln PO2B":PRINT #1,""
  FOR I = 1 TO n
    PRINT #1, RT(I),LPO2B(I)
  NEXT I
  PRINT #1,""
  CLOSE #1
340 PRINT:PRINT "Do you want to see a plot? Y/N"
980 ANS$ = FNUCASE$(INKEY$)
  IF ANS$="" GOTO 980
  IF ANS$ = "N" GOTO 301
  IF ANS$ <> "Y" GOTO 340
  FOR I = 1 TO N
    XIN(1,I) = RT(I)
    YIN(1,I) = PO2(I)
    XIN(2,I) = RT(I)
    YIN(2,I) = POB(I)
  NEXT I
  NSET = 2
  PRINT:PRINT "The following plot routines will use points."
  PRINT "Please specify symbols for points."
979 ANS$=INKEY$
  IF ANS$="" GOTO 979
  CALL SETUP(TITLE$,XLA$,YLA$,MAJX,MINX,YMAJ,YMIN,POIN$)
  CALL CONVERT(PXL,PXH,PYL,PYH,NSET,N)
  CLS
  CALL GMODE
  CALL CLRSCR
  CALL AXIS(MAJX,MINX,YMAJ,YMIN)
  CALL OOT(POIN$,NSET,N)

```

```

CALL SCALE(PXL,PXH,MAJX,PYL,PYH,YMAJ)
CALL LAB(TITLE$,XLA$,YLA$)
97B ANS$=INKEY$
   IF ANS$="" GOTO 97B
   CALL TMODE
301 PRINT:PRINT "Do you want to quit? Y/N"
977 ANS$=FNUCASE$(INKEY$)
   IF ANS$="" GOTO 977
   IF ANS$="Y" GOTO 290
   IF ANS$="N" GOTO 10
   GOTO 301
REM
REM SUBPROGRAM FOR LEAST SQUARE FITS
REM
SUB LEAST(N,M,B,SDM,SDB,RES,RESVAR,SE,NSET) STATIC
SX=0
SY=0
SXY=0
SXQ=0
SYQ=0
UZ=0
SUQ=0
SRES2=0
SZQ=0
FOR I=1 TO N
  SX=SX+XIN(NSET,I)
  SY=SY+YIN(NSET,I)
  SXQ=SXQ+XIN(NSET,I)*XIN(NSET,I)
  SYQ=SYQ+YIN(NSET,I)*YIN(NSET,I)
  SXY=SXY+XIN(NSET,I)*YIN(NSET,I)
NEXT I
D=N*(SXQ)-(SX*SX)
M=((N*SXY)-(SX*SY))/D
B=((SXQ*SY)-(SX*SXY))/D
REM COMPUTE CORRELATION COEFFICIENT, C
XA=SX/N
YA=SY/N
FOR I=1 TO N
  U=XIN(NSET,I)-XA
  Z=YIN(NSET,I)-YA
  UZ=UZ+U*Z
  SUQ=SUQ+U*U
  SZQ=SZQ+Z*Z
NEXT I
E=SUQ*SZQ
F=SQR(E)
C=UZ/F
REM COMPUTE STD. DEV. FOR SLOPE (SDM) AND FOR INTERCEPT (SDB)
VARY=(SZQ-(M*M*SUQ))/(N-2)
VARB=(VARY*SXQ)/(N*SUQ)
VARM=VARY/SUQ
SDB=SQR(ABS(VARB))
SDM=SQR(ABS(VARM))
REM FIND RESIDUALS [Y-YCALC] AND SUM SQUARES
FOR I=1 TO N
  RES(NSET,I)=YIN(NSET,I)-M*XIN(NSET,I)+B
  SRES2=SRES2+RES(NSET,I)*RES(NSET,I)
NEXT I
REM CALCULATE RESIDUAL VARIANCE AND STANDARD ERROR OF ESTIMATE
IF N= 2 THEN RESVAR = 1 ELSE RESVAR=SRES2/(N-2)
SE=SQR(RESVAR)
END SUB
REM
REM SUBPROGRAM SETUP IS USED TO INPUT LABELS, TICK MARKS, AND POINT SYMBOLS
REM
SUB SETUP(TITLE$,XLA$,YLA$,TXL,TXS,TYL,TYS,POIN$) STATIC
INPUT "What title would you like";TITLE$
INPUT "What label would you like on the X axis";XLA$
INPUT "What label would you like on the Y axis";YLA$

```

```

11 LONG = LEN(YLA$)
   IF LONG < 25 GOTO 15
   PRINT:PRINT "Label for Y axis is too long. Max. length is 25 characters."
   PRINT:PRINT "Enter new label for Y axis."
   INPUT YLA$
   GOTO 11
15 TXL = 10
   TXS = 10
   TYL = 10
   TYS = 10
   PRINT:PRINT "Default number of major ticks on X axis is "TXL
   PRINT "Default number of minor ticks on X axis is "TXS
   PRINT:PRINT "Default number of major ticks on Y axis is "TYL
   PRINT "Default number of minor ticks on Y axis is "TYS
   PRINT:PRINT "Major ticks are labeled on the axis and minors ticks are not."
   PRINT "Major ticks min. is 3 and max. is 10."
   PRINT "Minor ticks min. is 0 and max. is 10."
26 PRINT:PRINT "Do you wish to change these values? Y/N"
976 ANS$=FNUCASE$(INKEY$)
   IF ANS$="" GOTO 976
   IF ANS$ = "N" GOTO 42
   IF ANS$ <> "Y" GOTO 26
19 PRINT:INPUT "How many major ticks on the X axis";TXL
   IF TXL > 10 OR TXL < 3 GOTO 19
21 PRINT:INPUT "How many minor ticks on the X axis";TXS
   IF TXS > 10 GOTO 21
   IF TXS < 0 THEN TXS = 0
22 PRINT:INPUT "How many major ticks on the Y axis";TYL
   IF TYL > 10 OR TYL < 3 GOTO 22
23 PRINT:INPUT "How many minor ticks on the Y axis";TYS
   IF TYS > 10 GOTO 23
   IF TYS < 0 THEN TYS = 0
42 PRINT:PRINT "The plot routines are setup to handle three sets of
data"
   PRINT "The default symbol for plotting points will be circles."
   PRINT "You may choose any symbol from the keyboard to represent"
   PRINT "your point in the plot."
   PRINT:PRINT "Do you want to choose your own symbols? Y/N"
975 ANS$ = FNUCASE$(INKEY$)
   IF ANS$="" GOTO 975
   POIN$ = "000"
   IF ANS$ = "N" GOTO 31
   IF ANS$ <> "Y" GOTO 42
   FOR I = 1 TO 3
   PRINT:PRINT "What symbol would you like for data set number "I
974 ANS$ = INKEY$
   IF ANS$="" GOTO 974
   MID$(POIN$,I,1) = ANS$
   NEXT I
31 END SUB

REM
REM SUBPROGRAM CONVERT IS FOR THE CONVERSION OF REAL X AND Y COORDINATES
REM TO SCREEN X AND Y COORDINATES WITH VARIABLE LIMITS IN WINDOW
REM
SUB CONVERT(PXL,PXH,PYL,PYH,NLINE,N) STATIC
XLO = XIN(1,1)
XHI = XIN(1,1)
YLO = YIN(1,1)
YHI = YIN(1,N)
FOR I = 1 TO NLINE
FOR J = 1 TO N
IF XLO > XIN(I,J) THEN XLO = XIN(I,J)
IF XHI < XIN(I,J) THEN XHI = XIN(I,J)
IF YLO > YIN(I,J) THEN YLO = YIN(I,J)
IF YHI < YIN(I,J) THEN YHI = YIN(I,J)
NEXT J
NEXT I
32 PRINT:PRINT "Default X min is "XLO:PRINT "Default X max is "XHI
   PRINT:PRINT "Default Y min is "YLO:PRINT "Default Y max is "YHI

```



```

PRINT:PRINT "Do you wish to plot the default limits? Y/N"
973 ANS$ = FNUCASE$(INKEY$)
IF ANS$="" GOTO 973
IF ANS$ = "Y" GOTO 27
IF ANS$ <> "N" GOTO 32
PRINT:INPUT "Plot what value of X min";PXL
PRINT:INPUT "Plot what value of X max";PXH
PRINT:INPUT "Plot what value of Y min";PYL
PRINT:INPUT "Plot what value of Y max";PYH
FOR I = 1 TO NLINE
FOR J = 1 TO N
IF PXL < XIN(I,J) GOTO 62
NEXT J
62 ILO(I) = J - 1
IF ILO(I) < 1 THEN ILO(I) = 1
FOR J = 1 TO N
IF PXH > XIN(I,J) GOTO 82
NEXT J
82 IHI(I) = N + 1 - J
IF IHI(I) > N THEN IHI(I) = N
NEXT I
LO = PYL
HI = PYH
FOR J = 1 TO NLINE
FOR I = ILO(J) TO IHI(J)
IF LO > YIN(J,I) THEN LO = YIN(J,I)
IF HI < YIN(J,I) THEN HI = YIN(J,I)
NEXT I
NEXT J
IF PYL <= LO GOTO 102
103 PRINT:PRINT "Lower limit is too high, min value is "LO
INPUT "What is the new value of Y min";PYL
IF PYL > LO GOTO 103
102 IF PYH >= HI GOTO 43
131 PRINT:PRINT "Upper limit is too low, max value is "HI
INPUT "What is the new value of Y max";PYH
IF PYH < HI GOTO 131
GOTO 43
27 PXL = XLO
PXH = XHI
PYL = YLO
PYH = YHI
FOR J = 1 TO NLINE
ILO(J) = 1
IHI(J) = N
NP(J) = N
NEXT J
43 FOR J = 1 TO NLINE
NP(J) = IHI(J) - ILO(J) + 1
FOR I = ILO(J) TO IHI(J)
II = I - ILO(J) + 1
IX(J,II) = ((XIN(J,I) - PXL) * 600/(PXH - PXL)) + 84
IY(J,II) = 315 - ((YIN(J,I) - PYL) * 300/(PYH - PYL))
NEXT I
NEXT J
END SUB

REM
REM SUBPROGRAM AXIS IS TO DRAW THE X AND Y AXIS AND THE TICK MARK
REM DIVISIONS FOR SCALE
REM
SUB AXIS(TXL,TXS,TYL,TYS) STATIC
REM
REM Draws the X and Y axis
REM
IXA = 84
IYA = 15
CALL MOVE(IXA,IYA)
IYA = 315
CALL DLINE(IXA,IYA)

```

```

        IXA = 684
        CALL DLINE(IXA,IYA)
REM
REM  Draws tic marks on the Y axis
REM
        IXA = 84
        IYA1 = 87
        IF TYS = 0 GOTO 1001
        IN = 300 / (TYS * TYL)
        FOR I=1 TO TYS * TYL
            IYA = 15 + IN * (I-1)
            CALL MOVE(IXA,IYA)
            CALL DLINE(IXA1,IYA)
        NEXT I
1001 IXA = 89
        INN = 300 / TYL
        FOR I = 1 TO TYL
            IYA = 15 + INN * (I - 1)
            CALL MOVE(IXA1,IYA)
            CALL DLINE(IXA,IYA)
        NEXT I
REM
REM  Draws tic marks on the X axis
REM
        IYA = 315
        IYA1 = 312
        IF TXS = 0 GOTO 1002
        IN = 600 / (TXL * TXS)
        FOR I=1 TO TXL * TXS
            IXA = 84 + IN * (I-1)
            CALL MOVE(IXA,IYA)
            CALL DLINE(IXA,IYA1)
        NEXT I
1002 IYA = 310
        INN = 600 / TXL
        FOR I=1 TO TXL
            IXA = 84 + INN * (I-1)
            CALL MOVE(IXA,IYA1)
            CALL DLINE(IXA,IYA)
        NEXT I
        END SUB
REM
REM  SUBPROGRAM LAB IS TO LABEL THE TITLE, X AXIS, AND Y AXIS
REM
        SUB LAB(TITLE$,XLA$,YLABEL$) STATIC
        IXA = 110
        IYA = 13
        CALL TEXTB(IXA,IYA,TITLE$)
        ILEN = LEN(YLABEL$)
        IXA = 24
        IYA = 144 - ILEN * 5.5
        ILN = 1
        FOR I = 1 TO ILEN
            YLA$ = MID$(YLABEL$,I,ILN)
            IYA = IYA + 11
            CALL TEXTB(IXA,IYA,YLA$)
        NEXT I
        ILEN = LEN(XLA$)
        IYA = 340
        IXA = 384 - ILEN * 4.5
        CALL TEXTB(IXA,IYA,XLA$)
        END SUB
REM
REM  SUBPROGRAM SCALE IS TO LABEL EACH AXIS WITH THE SCALE
REM
        SUB SCALE(PXL,PXH,XMAX,PYL,PYH,YMAX) STATIC
        NVX = (PXH - PXL)/XMAX
        NVY = (PYH - PYL)/YMAX
        IN = 300 / YMAX

```

```

INN = 600 / XMAX
FOR I = 1 TO XMAX
XL$ = FNNUM$(PXL + (I - 1) * NVX)
LONG = LEN(XL$)
IXA = 84 - LONG * 4.5 + INN * (I - 1)
IYA = 328
CALL TEXTB(IXA,IYA,XL$)
NEXT I
FOR I = 1 TO YMAX
XL$ = FNNUM$(PYH - (I - 1) * NVY)
LONG = LEN(XL$)
IYA = 20 + IN * (I - 1)
IXA = 83 - 9 * LONG
CALL TEXTB(IXA,IYA,XL$)
NEXT I
END SUB

REM
REM SUBPROGRAM CURVE IS USED TO DRAW A CURVE FROM THE DATA
REM
SUB CURVE(N,NL) STATIC
CALL MOVE(IX(NL,1),IY(NL,1))
FOR I = 2 TO NP(NL)
CALL DLINE(IX(NL,I),IY(NL,I))
NEXT I
END SUB

REM
REM SUBPROGRAM STRAIGHT IS USED TO DRAW A STRAIGHT LINE FROM SLOPE
REM AND INTERCEPT CALCULATIONS
REM
SUB STRAIGHT(XMIN,XMAX,M,B,YMIN,YMAX) STATIC
Y = XMIN * M + B
ZY = 300 / (YMAX - YMIN)
ZX = 600 / (XMAX - XMIN)
IXMI = 84
IXMA = 684
IYMI = 315 - (Y - YMIN) * ZY
Y = XMAX * M + B
IYMA = 315 - (Y - YMIN) * ZY
IF IYMI > 15 GOTO 1100
IYMI = 15
X = (YMAX - B)/M
IXMI = 84 + (X - XMIN) * ZX
1100 IF IYMI < 315 GOTO 1110
IYMI = 315
X = (YMAX - B)/M
IXMI = 84 + (X - XMIN) * ZX
1110 IF IYMA > 15 GOTO 1120
IYMA = 15
X = (YMIN - B) / M
IXMA = 84 + (X - XMIN) * ZX
1120 IF IYMA < 315 GOTO 1130
IYMA = 315
X = (YMIN - B) / M
IXA = 84 + (X - MIN) * ZX
1130 CALL MOVE(IXMI,IYMI)
CALL DLINE(IXMA,IYMA)
END SUB

REM
REM SUBPROGRAM POINT IS USED TO PLOT A POINT WITH A SYMBOL
REM
SUB DOT(POIN$,NSET,N) STATIC
ILN = 2
FOR I = 1 TO NSET
PT$=MID$(POIN$,I,1)
IF PT$ = "O" GOTO 12
FOR J = 1 TO NP(I)
IPX = IX(I,J) - 4
IPY = IY(I,J) + 5
CALL TEXTB(IPX,IPY,PT$)

```

```
      NEXT J
      GOTO 29
12  FOR J = 1 TO NP(I)
      CALL CIRC(IX(I,J),IY(I,J),ILN)
      NEXT J
29  NEXT I
      END SUB
```

REFERENCES

1. Haggin, J. Chem. Eng. News (1988), 66, No. 28, 25.
2. Matson, S. Florida Advanced Materials Conference, Nov. 2, 1988, St. Augustine, FL.
3. Hsieh, H. P. New Membrane Materials and Processes for Separation, AICHE Symposium Series 261, 84, 1.
4. Leenaars, A. F. M.; Keizer, K.; Burggraaf, A. J. Chemtech (1986), 16, 560.
5. Nagamoto, H.; Inoue, H. Chem. Eng. Commun. (1985), 34, 315.
6. Khang, S. J.; Sun, Y. M. Ind. Eng. Chem. Res. (1988), 27, 1136.
7. Beaver, E. R.; Bhat, P. V. New Membrane Materials and Processes for Separations, AICHE Symposium Series 261, 84, 113.
8. Gienger, J. K.; Ray, R. J. New Membrane Materials and Processes for Separations, AICHE Symposium Series 261, 84, 168.
9. Ford, W. T. ed. Polymeric Reagents and Catalysts, ACS Symposium Series 308, American Chemical Society, Washington, DC, 1986.
10. Bergbreiter, D. E. Chemtech (1987), 17, 686.
11. Bayer, E.; Schurig, V. Angew. Chem. Int. Ed. (1975), 14, 493.
12. Pittman, C. U., Jr.; Smith, L. R.; Hanes, R. M. J. Amer. Chem. Soc. (1975), 97, 1742.
13. Wolynic, E. T.; Thompson, J. B.; Ollis, D. F. AICHE J. (1972), 18, 457.
14. Wolynic, E. T.; Ollis, D. F. Chemtech (1974), 4, 111.
15. Whitesides, G. M.; Bednarski, M. D.; Chenault, H. K.; Simon, E. S. J. Amer. Chem. Soc. (1987), 109, 1283.
16. Klibanov, A. Florida Catalysis Conference, May 1987, Palm Coast, FL.
17. Cheryan, M.; Mehaia, M. A. Chemtech (1986), 16, 676.

18. Waller, F. J. Polymeric Reagents and Catalysts, ACS Symposium Series 308, American Chemical Society, Washington, DC, 1986.
19. Waller, F. J.; Van Scoyoc, R. W. Chemtech (1987), 17, 438.
20. Barron, R. F. Cryogenic Systems, Oxford University Press, New York, 1985; 2nd ed.
21. Hands, B. A. Cryogenic Engineering, Academic Press, London, 1986.
22. Braton, N. R. Cryogenic Recycling and Processing, CRC Press, Boca Raton, FL, 1980.
23. Knoblauch, K. Chemical Engineering (Nov. 6, 1978), 87.
24. Miwa, K.; Inoue, T. Chemical Economy and Engineering Review (1980), 12, 40.
25. Whyte, Jr., T. E.; Yon, C. M.; Wagener, E. H. Industrial Gas Separations, ACS Symposium Series 223, American Chemical Society, Washington, DC, 1983.
26. Stern, S. A.; Frisch, H. L. Ann. Rev. Mater. Sci. (1981), 11, 523.
27. Meares, P. Membrane Separation Processes, Elsevier Scientific Publishing Co., Amsterdam, 1976.
28. Lloyd, D. R. Materials Science of Synthetic Membranes, ACS Symposium Series 269, American Chemical Society, Washington, DC, 1985.
29. Haggin, J. Chem. Eng. News (1985), 63, 26.
30. Haggin, J. Chem. Eng. News (1988), 66, 7.
31. Beaver, E. R.; Bhat, P. V. New Membrane Materials and Processes for Separations, AIChE Symposium Series 261, 84, 113.
32. Gienger, J. K.; Ray, R. J. New Membrane Materials and Processes for Separations, AIChE Symposium Series 261, 84, 168.
33. Graham, T. Phil. Trans. Roy. Soc. (1854), 144, 177.
34. Graham, T. Phil. Trans. Roy. Soc. (1863), 153, 385.
35. Graham, T. Phil. Mag. and J. of Science Series 4 (1866), 32, 401.
36. Schultz, J. S.; Soddard, J. D.; Suchdeo, S. R. AIChE J. (1974), 20, 417.

37. Smith, D. R.; Lander, R. J.; Quinn, J. A. Rec. Dev. Sep. Sci. (1977), 3, 225.
38. Way, J. D.; Noble, R. D.; Flynn, T. M.; Sloan, E. D. J. Membrane Sci. (1982), 12, 239.
39. Kimura, S. G.; Matson, S. L.; Ward, III, W. J. Rec. Dev. Sep. Sci. (1979), 5, 11.
40. Drago, R. S.; Corden, B. B. Acc. Chem. Res. (1980), 13, 353.
41. Tsumaki, T. Bull. Chem. Soc. Jpn. (1938), 13, 252.
42. Roman, I. C.; Baker, R. W. U.S. Patent No. 4,542,010, 1985.
43. Sterzel, H. J.; Sanner, A. Ger. Offen. DE No. 3,407,149, 1985, C.A. 104:110951j.
44. Nishide, H.; Kuwahara, M.; Ohyanagi, M.; Funada, Y.; Kawakami, H.; Tsuchida, E. Chem. Lett. (1986), 43.
45. Drago, R. S.; Gaul, J. H.; Zombeck, A.; Straub, D. K. J. Am. Chem. Soc. (1980), 102, 1033.
46. Nishide, H.; Ohyanagi, M.; Okada, O.; Tsuchida, E. Macromolecules (1986), 19, 494.
47. Nishide, H.; Ohyanagi, M.; Okada, O.; Tsuchida, E. Macromolecules (1987), 20, 417.
48. Tsuchida, E.; Nishide, H.; Ohyanagi, M.; Kawakami, H. Macromolecules (1987), 20, 1907.
49. Nishide, H.; Ohyanagi, M.; Kawakami, H.; Tsuchida, E. Bull. Chem. Soc. Jpn. (1986), 59, 3213.
50. Drago, R. S.; Balkus, K. J., Jr. Inorg. Chem. (1986), 25, 716.
51. Barnes, M. J.; Drago, R. S.; Balkus, K. J., Jr. J. Am. Chem. Soc. (1988), 110, 6780.
52. Pribich, D. C. Ph.D. Dissertation, University of Florida, 1985.
53. Paterson, C. M. J. Appl. Polym. Sci. (1968), 12, 2649.
54. Yashuda, H.; Rosengren, K. J. J. Appl. Polym. Sci. (1970), 14, 2839.
55. Salame, M. J. Polym. Sci. (1973), 41, dl.
56. Stannett, V. T. Polym. Eng. Sci. (1978), 18, 1129.

57. Kawakami, Y.; Karasawa, H.; Kamiya, H.; Aoki, T.; Yamashita, Y. Polym. J. (1986), 18, 237.
58. Carre, A.; Gamet, D.; Schultz, J.; Schreiber, H. P. J. Macromol. Sci., Chem. (1986), A23, 1.
59. Chainey, M.; Wilkinson, M. C.; Hearn, J. J. Polym. Sci. (1985), 23, 2947.
60. Chern, R. T. Ph.D. Dissertation, North Carolina State University, 1983.
61. Drago, R. S.; Cannady, J. P.; Leslie, K. A. J. Am. Chem. Soc. (1980), 102, 6014.
62. Drago, R. S.; Gaul, J. H. Inorg. Chem. (1979), 18, 2019.
63. Kirschenbaum, I.; Inchalik, E. J. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Wiley-Interscience Publications, New York, 1977, 16, 637.
64. Pruett, R. L. Advances in Organometallic Chemistry (1979), 17, 1.
65. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987, 2nd ed.
66. Wilkinson, G.; Evans, D.; Yagupsky, G. J. Chem. Soc. (A) (1968), 2660.
67. Wilkinson, G.; Evans, D.; Osborn, J. A. J. Chem. Soc. (A) (1968), 3133.
68. Wilkinson, G.; Brown, C. K. Tetrahedron Letters (1969), 22, 1725.
69. Wilkinson, G.; Yagupsky, M.; Brown, C. K.; Yagupsky, G. J. Chem. Soc. (A) (1970), 937.
70. Wilkinson, G.; Yagupsky, G.; Brown, C. K. J. Chem. Soc. (A) (1970), 1392.
71. Wilkinson, G.; Brown, C. K. J. Chem. Soc. (A) (1970), 2753.
72. Sheldon, R. A.; Kochi, J. K. Metal Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981.
73. Mimoun, H. "Metal Complexes in Oxidation" in Comprehensive Coordination Chemistry, 6, Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds. Pergamon Press, Oxford, 1987.
74. Spiro, T. G. Metal Ion Activation of Dioxygen, John Wiley and Sons, New York, 1980.

75. Tabushi, I. Coord. Chem. Rev. (1988), 86, 1.
76. Dudley, C.; Read, G. Tetrahedron Letters (1972), 52, 5273.
77. Dudley, C.; Read, G.; Walker, P. J. C. J. Chem. Soc. Dalton Trans. (1974), 1926.
78. Read, G.; Walker, P. J. C. J. Chem. Soc., Dalton Trans. (1977), 883.
79. Mimoun, H.; Machirant, M. M. P.; Serey de Roch, I. J. Amer. Chem. Soc. (1978), 100, 5437.
80. Drago, R. S.; Nyberg, E. D. J. Amer. Chem. Soc. (1981), 103, 4968.
81. Drago, R. S.; Nyberg, E. D.; Pribich, D. C. J. Amer. Chem. Soc. (1983), 105, 3538.
82. Drago, R. S.; Zuzich, A.; Nyberg, E. D. J. Amer. Chem. Soc. (1985), 107, 2898.
83. Oae, S.; Organic Chemistry of Sulfur, Plenum, New York, 1977, Chapter 8.
84. Szmant, H. H.; Lapinski, R. J. Amer. Chem. Soc. (1958), 80, 6883.
85. Djerassi, C.; Engle, R. R. J. Amer. Chem. Soc. (1953), 75, 3838.
86. Henbest, H. B.; Khan, S. A. J. Chem. Soc., Chem. Commun. (1968), 1036.
87. Kuhn, L. Angew. Chem. (1966), 78, 957.
88. Curci, R.; DiFuria, F.; Testi, R.; Modena, G. J. Chem. Soc., Perkin Trans. II (1977), 576.
89. Curci, R.; DiFuria, F.; Modena, G.; Cenci, S.; Edwards, J. O. J. Chem. Soc., Perkin Trans. II (1978), 979.
90. Schultz, H. S.; Freyermuth, H. B.; Buc, S. R. J. Org. Chem. (1963), 28, 1140.
91. Ganear, B.; Heggs, R. D.; Biloski, A. J.; Schwartz, J. Tetrahedron Letters (1980), 21, 685.
92. Kahr, K.; Berther, C. Chem. Berichte (1960), 93, 132.
93. Drabowicz, J.; Mikolajczyk, M. Synthesis (1978), 758.
94. Ledlie, M. A.; Howell, I. V. Tetrahedron Letters (1976), 10, 785.

95. Ledlie, M. A.; Howell, I. V.; Pitkethly, R. C. British Patent No. 1404513, (1975).
96. Muller, P.; Godoy, J. Helv. Chim. Acta (1983), 66, 1790.
97. Ledlie, M. A.; Howell, I. V.; Allum, K. G.; Pitkethly, R. C. J. Chem. Soc., Perkin Trans. I (1976), 1734.
98. Riley, D. P. Inorg. Chem. (1983), 22, 1965.
99. Riley, D. P.; Shumate, R. E. J. Amer. Chem. Soc. (1984), 106, 3179.
100. Riley, D. P.; Oliver, J. D. Inorg. Chem. (1986), 25, 1814.
101. Bailey, C. L.; Drago, R. S. J. Chem. Soc., Chem. Commun. (1987), 179.
102. Groves, J. T.; Quinn, R. J. Amer. Chem. Soc. (1985), 107, 5790.
103. Moyer, B. A.; Sipe, B. K.; Meyer, T. J. Inorg. Chem. (1981), 20, 1475.
104. Ellis, C. D.; Gilbert, J. A.; Murphy, W. R.; Meyer, T. J. J. Amer. Chem. Soc. (1983), 105, 4842.
105. Drago, R. S.; Davis, S.; Bilgrien, C. J. Amer. Chem. Soc. (1987), 109, 3786.
106. Drago, R. S.; Barnes, M. J.; Davis, S.; Ramsden, J. H.; Bailey, C. L. 1987 U. S. Army C.R.D.E.C. Conference on Chemical Defense, Aberdeen, MD.
107. Drago, R. S. 1986 - 1987 U. S Army C.R.D.E.C. Annual Report, Univ. of Florida Technology Center, Gainesville, FL, 1987.
108. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Wiley-Interscience Publications, New York, 1977, 13, 16.
109. Gosser, L. W. U. S. Patent No. 726695, (1985).
110. Stinson, S. Chem. Eng. News (1987), 67, 14.
111. Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. Inorganic Syntheses XV, 45.
112. Getty, C. S. Ph.D. Dissertation, University of Florida, 1988.
113. Robinson, S. D.; Dobson, A.; Uttley, M. F. J. Chem. Soc., Dalton Trans. (1975), 370.
114. Drago, R. S.; Telser, J. Inorg. Chem. (1984), 23, 2599.

115. Collin, J. P.; Sauvage, J. P. Inorg. Chem. (1986), 25, 135.
116. Wilkinson, G.; Spencer, A. J. Chem. Soc., Dalton Trans. (1972), 1570.
117. Roelen, O. German Patent No. 849548, (1938).
118. Pruett, R. L.; Smith, J. A. J. Org. Chem. (1969), 34, 327.
119. Brewester, E. A. V. Chemical Engineering (Nov. 8, 1976), 83, 90.
120. Brewester, E. A. V. Chemical Engineering (Dec. 5, 1977), 84, 110.
121. Craddock, J. H.; Hershman, A.; Paulik, F. E.; Roth, J. F. Ind. Eng. Chem., Prod. Res. Dev. (1969), 8, 291.
122. Parshall, G. W. Homogeneous Catalysis: The Application and Chemistry of Catalysis by Soluble Transition Metal Complexes, John Wiley and Sons, New York, 1980, Chapter 5.
123. Collman, J. P.; Belmont, J. A.; Brauman, J. I. J. AM. Chem. Soc. (1983), 105, 7288.
124. Fritschel, S. J.; Ackerman, J. J. H.; Keyser, T.; Stille, J. K. J. Org. Chem. (1979), 44, 3152.
125. Bechtold, M. F.; Mahler, W.; Schunn, R. A. J. Polymer Sci., Polymer Chem. Ed. (1980), 18, 2823.
126. Abatjoglou, A. G.; Billig, E.; Bryant, D. R. Organometallics (1984), 3, 932.
127. Garrou, P. Chem Rev. (1985), 85, 171.
128. Arai, H.; Kaneko, T.; Kunugi, T. Chem. Lett. (1975), 265.
129. Robinson, K. K.; Paulik, F. E.; Hershman, A.; Roth, J. F. J. Catal. (1969), 15, 245.
130. Arai, H.; Tominaga, H. J. Catal. (1982), 75, 188.
131. Takahashi, N.; Kobayashi, M. J. Catal. (1984), 85, 89.
132. Davis, M.; Rode, E.; Taylor, D.; Hanson, B. E. J. Catal. (1984), 86, 67.

BIOGRAPHICAL SKETCH

Mark J. Barnes was born in Towanda, Pennsylvania, on July 20, 1962. He graduated with honors from Towanda High School in June 1980 and attended Ithaca College in Ithaca, New York, that fall. The next year he was elected into the Oracle Society, a freshman honor society, and later became a member of both the honor societies of Phi Kappa Phi and Sigma Xi, the Scientific Research Society. At Ithaca College, he conducted research in the area of synthetic organic chemistry under the supervision of Dr. Heinz F. Koch. He presented papers based on this work at both the Eastern College's Science Conference and the Middle Atlantic Regional Meeting of the American Chemical Society. He graduated with honors from Ithaca College in May 1984.

In August 1984, he entered the University of Florida as a graduate student and joined the research group of Dr. Russell S. Drago. While at Florida, he presented papers at the Florida Conference on Catalysis, Florida Advanced Materials Conference, the 1987 Middle Atlantic Regional Meeting of the American Chemical Society, the 1987 Southeast Regional Meeting of the American Chemical Society, and the 1987 National Meeting of the American Chemical Society in New Orleans.

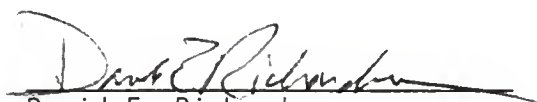
The author has published one paper in the Journal of the American Chemical Society and is currently preparing two others for publication. Upon receiving the degree of Doctor of Philosophy, he plans to begin his career with Savannah River Laboratories in Aiken, South Carolina.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



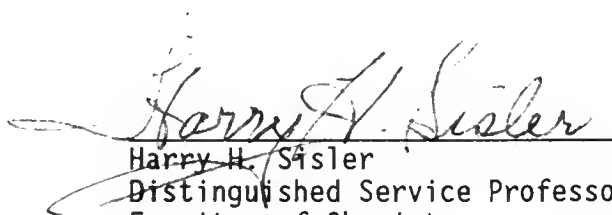
Russell S. Drago
Graduate Research Professor
of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



David E. Richardson
Associate Professor of
Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



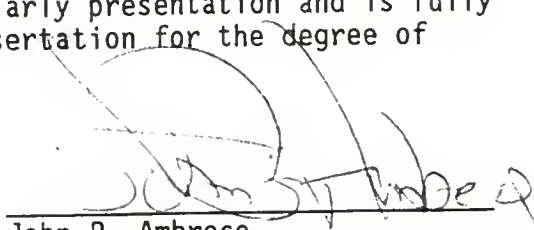
Harry H. Sisler
Distinguished Service Professor
Emeritus of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



William M. Jones
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



John R. Ambrose
Associate Professor of
Materials Science and
Engineering

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 1989

Dean, Graduate School

UNIVERSITY OF FLORIDA



3 1262 08554 2776